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(54) Method of processing silver halide color photographic light-sensitive materials

Verfahren zur Verarbeitung farbphotographischer lichtempfindlicher Silberhalogenidmaterialien

Procédé de traitement des matériaux photosensibles pour la photographie en couleur

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- **PATENT ABSTRACTS OF JAPAN vol. 14, no. 321**
(P-1074)(4264) 10 July 1990 & JP-A-2 105 148
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(P-1043)(4150) 26 April 1990 & JP-A- 2 046 448
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- **US-A-5 001 506**
- **& JP-A-2 168 253 (FUJI PHOTO FILM CO. LTD.)**
- **& JP-A-2 170 161 (...)**

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Description**BACKGROUND OF THE INVENTION**

5 The present invention relates to a method of processing silver halide color photographic light-sensitive materials. More particularly, the present invention relates to a processing method which is capable of rapid-processing, low in replenishing volume, improved in desilverizing capability, and excellent in processing stability.

In forming color images by photographic processing of an imagewise-exposed light-sensitive material, a desilvering process followed by a washing process or stabilizing process is generally provided after a color developing process. 10 In recent years, light-sensitive materials have come to be processed in automatic processing machines installed in processing laboratories. In such processing laboratories, customers demand prompt service so that processing of light-sensitive materials is completed, and materials are returned on the same day they are brought in for processing; recently, return within hours has come to be requested. Accordingly, a technological development in rapid processing is desired.

15 Under the circumstances, Eastman Kodak Company proposes a rapid processing for color paper called Process RA-4, which performs processing in 3 minutes at 35°C by three steps comprising color developing of 45 seconds, bleach-fixing of 45 seconds and stabilizing of 90 seconds.

The prior art aimed at a rapid processing of light-sensitive materials can be roughly classified into three types, namely

- (1) techniques to improve light-sensitive materials,
- (2) techniques relating to mechanical means in processing, and
- (3) techniques to improve the composition of a processing solution used in processing.

25 The above (1) includes [1] improvement in silver halide composition (for example, a technique to minimize the size of silver halide grains as described in Japanese Pat. O.P.I. Pub. No. 77223/1976 and a technique concerning silver halide having a low bromide content described in Japanese Pat. O.P.I. Pub. No. 18142/1983 and Japanese Pat. Examined Pub. No. 18939/1981), [2] use of additives (for example, a technique to add 1-aryl-3-pyrazolidone having a specific structure to a light-sensitive material as described in Japanese Pat. O.P.I. Pub. No. 64339/1981 and a technique 30 to add 1-arylpyrazolidones to a light-sensitive material as described in Japanese Pat. O.P.I. Pub. Nos. 144547/1982, 50534/1983, 50535/1983 and 50536/1983), [3] techniques based on rapid reactive couplers (for example, couplers as described in Japanese Pat. Examined Pub. No. 10783/1976 and Japanese Pat. O.P.I. Pub. Nos. 123342/1975, 102636/1976), and [4] techniques relating to a photographic thin-layered structure (for example, a technique relating to thinned photographic component layers described in Japanese Pat. Application No. 204992/1085).

35 The above (2) includes techniques for stirring a processing solution (for example, a stirring technique described in Japanese Pat. Application No. 23334/1986).

The above (3) includes [1] techniques using developing accelerators, [2] techniques using high-concentration color developing agents and [3] techniques for reducing the concentration of halide ions, especially bromide ions.

In these rapid processing techniques, use of light-sensitive material containing a silver halide having a high silver chloride content (a technique described, for example, in Japanese Pat. O.P.I. Pub. Nos. 95345/1983, 19140/1985 and 95736/1983), which falls into (1) above, can provide a particularly high rapid processability.

Rapid processing achieved by raising desilverizing speed in a desilvering process is also known. As bleaching agents used in desilverization, there have been used oxidizing agents such as ferricyanates, bichromates, persulfates and ferric chloride. However, these oxidizing agents may pollute the environment; moreover, these are difficult to reuse 45 by recovery, and thereby used processing solutions must be disposed of as waste.

To solve such a pollution problem as well as to meet the requirements for rapid and easy processing and for capability of recycling waste solutions, there has come to be widely used a processing solution containing an (ethylenediaminetetracetato) ferric complex salt as an oxidizing agent. The processing solution using a (ethylenediamine-tetracetato) ferric complex salt has disadvantage that the bleaching speed is low owing to the complex salt's slow 50 oxidizing capability.

Though a longer processing time can prevent poor desilverization, this is contradictory to the requirement for rapid processing.

As another method of rapid processing, the so-called bleach-fixing monobath in which a bleacher solution and fixer solution are mixed in one solution is practiced. And as a means to accelerate the desilverization, a method of 55 using a (diethylenetriaminepentacetato) ferric complex salt is disclosed in Japanese Pat. O.P.I. Pub. No. 149358/1984.

Further, Japanese Pat. O.P.I. Pub. No. 222252/1986 discloses a method including the use of ferric complex salts of diethylenetriamine pentacetic acid, cyclohexanediaminetetracetic acid and 1,3-diaminopropane tetracetic acid in combination therewith.

When a ferric diethylenetriamine pentacetate complex salt is used in a one-bath bleach-fix solution, the desilverization speed is increased as compared with the use of a ferric diethylenetriamine tetracetate complex salt; but, it is still insufficient.

Further, when ferric complex salts of diethylenetriaminepentacetic acid, cyclohexanediamine tetracetic acid and 1,3-diaminopropane tetracetic acid are jointly used in a bleach-fixing bath, precipitation of sulfides occurs because the oxidation capability of a (1,3-diaminopropanetetracetato) ferric complex salt is too strong. As a result, the fixing capability is lowered; and when the replacement by a replenishing solution is low, tar tends to be generated and the amount of yellow stain is liable to increase.

EP-A-0429940, which falls within the terms of Article 54(3) EPC, discloses a method for processing a silver halide light sensitive material having a silver chloride content of 90 mol% or more. The material is colour developed in a colour developing solution containing a hydrophilic p-phenylenediamine derivative and is then subjected to bleaching or bleach fixing. There is no reference in EP-A-0429940 of the use of a compound of formula E as described herein, or of a bleaching time of no longer than 40 seconds.

JP-A-2168253 discloses a system for wet processing a first and a second colour photosensitive material, the processing route comprising transfer means for passing certain of the processing solutions between the paths for the first and second materials. The colour developers used in accordance with JP-A-2168253 do not include a compound of formula E as used herein. Nor is there any disclosure of a processing time with a bleaching solution of 40 seconds or less.

EP-A-0438156, which falls within the terms of Article 54(3) EPC, discloses a method for processing silver halide colour photographic materials, which method comprises a washing step and replenishment of the wash water. The developing solution used in EP-A-0438156 does not include a compound of formula E as disclosed herein.

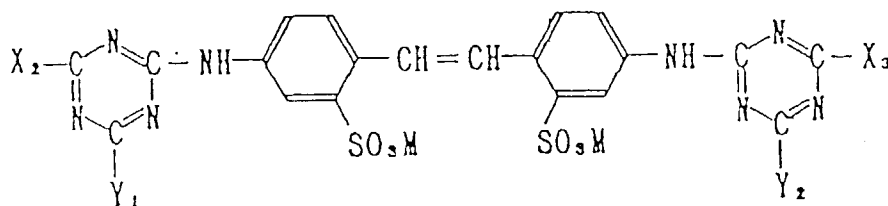
EP-A-0329088 relates to a processing method for a silver halide colour photographic light sensitive material which includes a bleaching step. The method of EP-A-0329088 is not specifically designed to be used with a light sensitive material having a high silver chloride content of at least 80 mol%. Nor is there any reference in EP-A-0329088 to the use of a compound of formula E as set out herein in a developing solution.

SUMMARY OF THE INVENTION

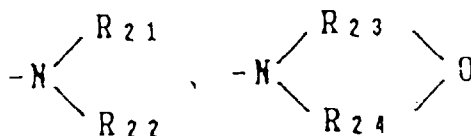
An object of the present invention is to provide a method of processing silver halide colour photographic light-sensitive materials which is improved in desilverizing in rapid processing, can reduce a replenishing volume and lower a pollution load, and possesses excellent processing stability which allows both continuous processing and small-batch processing over a long period of time.

The present inventors have made an intensive study and have found that the above objects are attained by a method of processing a silver halide colour photographic light-sensitive material, wherein a silver halide colour photographic light-sensitive material comprising at least one silver halide emulsion layer containing silver halide grains having a silver chloride content of not less than 80 mol% is colour developed with a colour developer comprising a compound represented by the following Formula E,

Formula (E)



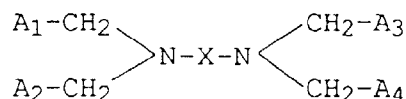
wherein X², X³, Y₁ and Y₂ each independently represent a hydroxyl group, halogen atom, alkyl group, aryl group,



or -OR₂₅, wherein R₂₁ and R₂₂ each independently represent a hydrogen atom, alkyl group or aryl group; R₂₃ and R₂₄

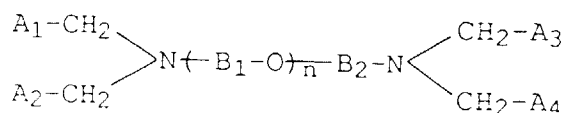
each represent an alkylene group; R_{25} represents a hydrogen atom, alkyl group or aryl group; and M represents a cation; processing the colour-developed material with a bleaching solution (BL-1) for a processing time of no longer than 40 seconds, the bleaching solution comprising at least one ferric complex salt of an organic acid represented by the following formula [A] or [B]:

Formula [A]



wherein A_1 to A_4 which may be the same or different, represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$; M, M_1 and M_2 individually represent hydrogen atom, alkali metal or ammonium; and X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms, and

Formula [B]



wherein A_1 to A_4 are the same as those defined for Formula [A]; n represents an integer from 1 to 8; and B_1 and B_2 , which may be the same or different, represent substituted or unsubstituted alkylene groups having 2 to 5 carbon atoms, and wherein the bleaching solution (BL-1) is replenished in an amount of not more than 50 ml/m² of photographic material processed.

With regard to the foregoing, the present inventors have also found that the above object is attained most effectively, when at least one ferric complex salt of the organic acid represented by Formula [A] or [B] is present in a concentration of not less than 0.1 mol per litre of bleacher solution, that the pH of said bleaching solution is not more than 5.5, that the replenishing solution of said bleaching solution comprises a portion or the total of an overflowed bleaching solution which has processed different kinds of silver halide colour photographic light-sensitive materials, and/or that the amount of silver in said silver halide colour photographic light sensitive material is not more than 0.75 g/m².

The object of the invention is attained by using a silver-chloride-rich light-sensitive material and a ferric complex salt of a highly oxidative organic acid including 1,3-diaminopropane tetracetic acid and represented by Formula [A], or a ferric complex salt of an organic acid including glycoether diamine tetracetic acid and represented by Formula [B], and by separating the bleaching process from the fixing process. It is not entirely clear why generation of tar can be prevented and why staining can be prevented.

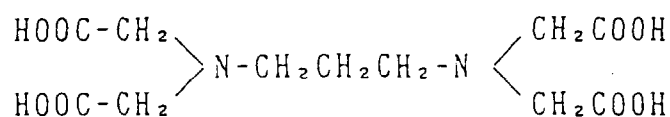
According to the invention, the bleaching solution contains at least one ferric complex salt of the organic acid represented by Formula [A] or [B] as a bleaching agent.

The compound represented by Formula [A] is described in detail below:

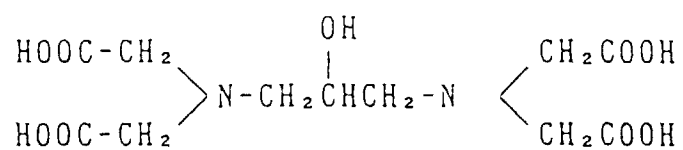
In Formula [A], A_1 to A_4 , which may be the same or different, represent $-CH_2OH$, $-COOM$ or $-PO_3M_1M_2$; M, M_1 and M_2 independently represent a hydrogen atom, alkali metal (for example, sodium, potassium) or ammonium. X represents a substituted or unsubstituted alkylene group having 3 to 6 carbon atoms (for example, propylene, butylene, pentamethylene). Substituents are such as hydroxyl group and alkyl groups having 1 to 3 carbon atoms.

Preferred examples of the compound represented by Formula [A] are as follows:

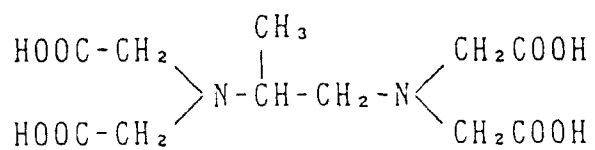
(A - 1)



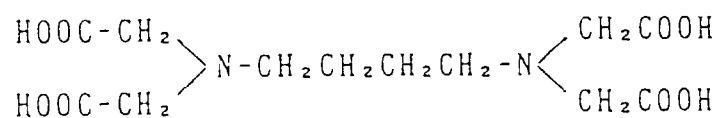
(A - 2)



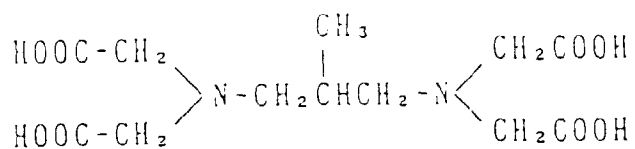
(A - 3)



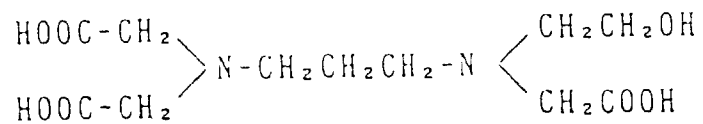
(A - 4)



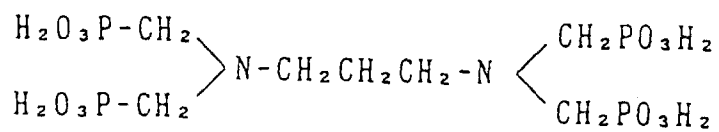
(A - 5)



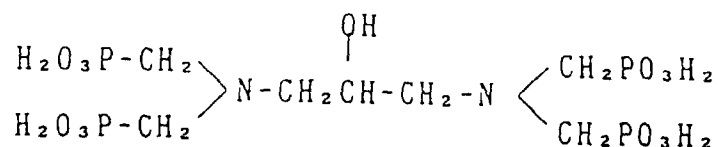
(A - 6)



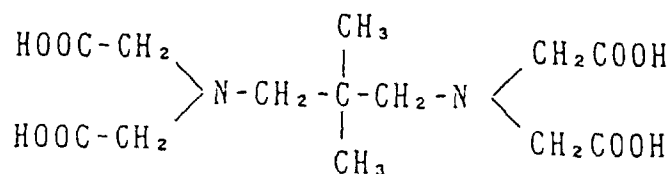
(A - 7)



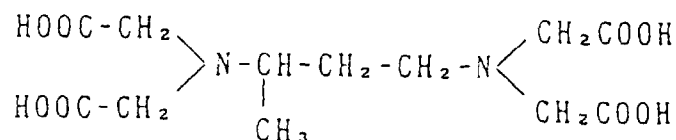
(A - 8)



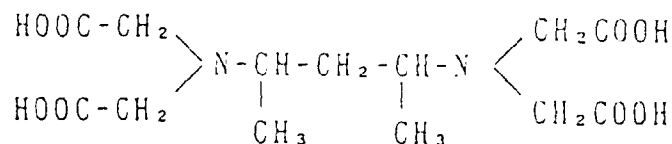
(A - 9)



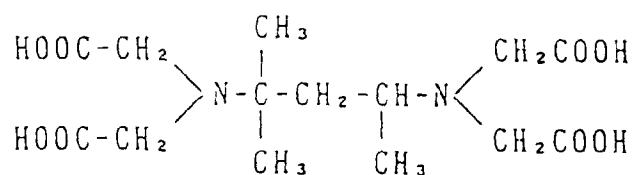
(A - 10)



(A - 11)



(A - 12)



As ferric complex salts of (A-1) to (A-12), there may be used any of sodium salt, potassium salt and ammonium salts of the ferric complexes. But, in view of the purpose of the invention and solubilities of these ferric complexes, ammonium salts and potassium salts are preferred.

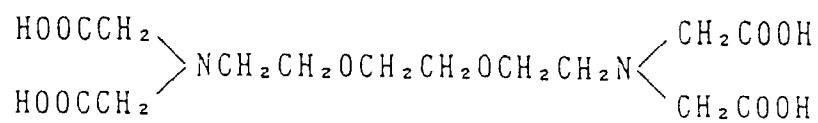
Among the above exemplified compounds, (A-1), (A-3), (A-4), (A-5) and (A-9) are preferably used in the invention; (A-1) is particularly preferred.

Next, the compound represented by Formula [B] is described in detail.

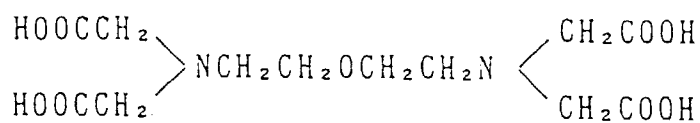
In Formula [B], A¹ to A⁴ are the same as the above, n represents an integer from 1 to 8, and B¹ and B² may be the same or different and represent substituted or unsubstituted alkylene groups (for example, ethylene, propylene, butylene, pentamethylene). Substituents are such as hydroxyl groups or lower alkyl groups having 1 to 3 carbon atoms (for example, methyl, ethyl, propyl).

Preferred examples of the compound represented by Formula [B] are as follows:

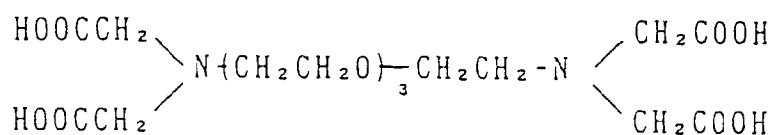
(B - 1)



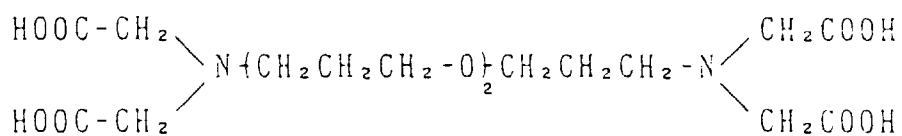
(B - 2)



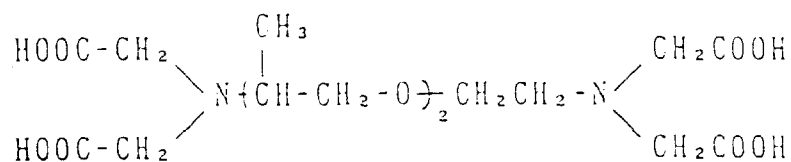
(B - 3)



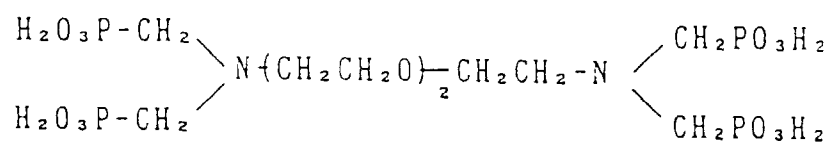
(B - 4)



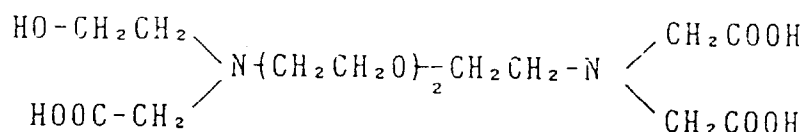
(B - 5)



(B - 6)



(B - 7)



As ferric complex salts of (B-1) to (B-7), there may be used any of sodium salt, potassium salt and ammonium salt of the ferric complexes.

Among the above exemplified compounds, (B-1), (B-2) and (B-7) are preferably used in the invention; (B-1) is particularly preferred.

The ferric complex salt of the organic acid represented by Formula [A] or [B] is contained generally in an amount of not less than 0.1 mol, preferably in a range from 0.2 to 1.5 mol per liter of the bleaching solution.

In the bleaching solution, ferric complex salts (for example, ammonium, sodium, potassium and triethanolamine salts) of the following compounds may be used as bleaching agents together with the compounds represented by Formula [A] or [B].

- [A'-1] Ethylenediamine tetracetic acid
- [A'-2] Trans-1,2-cyclohexanediamine tetracetic acid
- [A'-3] Dihydroxyethyl
- [A'-4] Ethylenediamide tetrakis(methylene phosphonic acid)
- [A'-5] Nitrilotrismethylene phosphonic acid
- [A'-6] Diethylenetriamine pentakis(methylene phosphonic acid)
- [A'-7] Diethylenetriamine pentacetic acid
- [A'-8] Ethylenediamine diorthohydroxyphenyl acetic acid
- [A'-9] Hydroxyethylethylenediamine triacetic acid
- [A'-10] Ethylenediamine dipropionic acid
- [A'-11] Ethylenediamine diacetic acid
- [A'-12] Hydroxyethyliminodiacetic acid
- [A'-13] Nitrilotriacetic acid
- [A'-14] Nitrilotripropionic acid
- [A'-15] Triethylenetetramine hexacetic acid
- [A'-16] Ethylenediamine tetrapropionic acid

These organic acid ferric complex salts may be used in the form of a complex salt, or a ferric complex ion may be formed in the solution using a ferric salt such as ferric sulfate, ferric chloride, ferric acetate, ammonium ferric sulfate, ferric phosphate, and an aminopolycarboxylic acid or salt thereof. When employed in the form of a complex salt, they may be used singly or in combination. In case complex ions are formed in the solution from ferric salts and aminopolycarboxylic acids, ferric salts may be used singly or in combination of two or more kinds; aminopolycarboxylic acids may be also used singly or in combination of two or more kinds. In both cases, aminopolycarboxylic acids may be used in excess of an amount necessary to form ferric ion complex salts.

Further, in a bleaching solution containing the above ferric complex salt, there may coexist complex salts of metal ions other than ferric ions, such as cobalt, copper, nickel and zinc ions.

Moreover, rapid processability can be improved by adding to the bleaching solution at least one of imidazole compounds or their derivatives described in the specification of Japanese Pat. Application No. 48931/1988, or compounds represented by Formulae [I] to [IX] described in the same specification or their exemplified compounds.

In addition to the above bleaching accelerators, there may be used for the same purpose compounds exemplified on pages 51 to 115 of the specification of Japanese Pat. Application No. 263568/1985, compounds exemplified on pages 22 to 25 of the specification of Japanese Pat. O.P.I. Pub. No. 17445/1988, and compounds described in Japanese Pat. O.P.I. Pub. Nos. 95630/1978 and 28426/1978.

These bleaching accelerators may be used singly or in combination. The addition amount is generally in a range of about 0.01 to 100 g, preferably 0.05 to 50 g, and especially 0.05 to 15 g per liter of the bleacher solution.

In general, these bleaching accelerators are dissolved in water, alkalis or organic acids prior to addition, but they may be added as they are; organic solvents such as methanol, ethanol and acetone may be used when necessary.

The pH of the bleaching solution is generally not more than 5.5, preferably 2.5 to 5.5.

This pH is that of a working solution in which a silver halide light-sensitive material is being processed and is clearly

distinguished from that of a replenishing solution.

The temperature of the bleaching solution is in a range of 20 to 50°C, preferably 25 to 45°C.

The processing time in the bleaching solution is not longer than 40 seconds, preferably not longer than 30 seconds and especially not longer than 25 seconds; therefore, the effect of the invention becomes more remarkable in rapid processing. The term "processing time in the bleaching solution" means a time from when the head of a light-sensitive material starts to dip into the bleaching solution till the head comes out of the bleaching solution.

In general, the bleaching solution uses halides such as ammonium bromide, potassium bromide and sodium bromide. Fluorescent brighteners, defoamers and surfactants may also be added thereto.

The replenishing volume of the bleaching solution for color paper is not more than 50 ml, preferably not more than 30 ml per square meter of a light-sensitive material. For color negative film, it is generally not more than 180 ml and preferably not more than 140 ml per square meter of a light-sensitive material. The effect of the invention becomes more evident as the replenishing volume decreases.

It is preferable that a portion or all of the replenishing solution for the bleacher solution be composed of an overflowed bleaching solution which has processed different kinds of silver halide color photographic light-sensitive materials.

Specifically in a dual-processing line using bleaching baths A and B, for example, the overflowed bleacher solution from bleaching bath A is utilized as a replenishing solution for bleaching bath B.

Light-sensitive materials to be processed in bleaching baths A and B have only to be different in kind. There may be various combinations of light-sensitive materials, such as color negative film and color paper; color negative film or color paper and color reversal film or paper; color negative films which differ in AgCl content, AgBr content or sensitivity; and color papers which differ in AgCl content, AgBr content or sensitivity. Of them, a combination of color negative film and color paper is particularly preferred in the invention. In the invention, activity of the bleacher solution may be enhanced, if desired, by blowing air into the processing bath or replenishing solution tank, or by adding thereto suitable oxidizing agents such as hydrogen peroxide, bromates or persulfates.

Next, there will be described a fixer solution used in the fixing process which may follow the bleaching process.

As fixing agents contained in the fixer solution, thiosulfates and/or thiocyanates are preferably used. The addition amount of thiosulfates is preferably not less than 0.4 mol/l, and that of thiocyanates is preferably not less than 0.5 mol/l.

Besides these fixing agents, the fixer solution may contain, singly or in combination, pH buffers comprising various compounds such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium bicarbonate, acetic acid, sodium acetate and ammonium hydroxide.

There may be preferably added to the fixer solution, in large amounts, halogenation agents comprising alkalimetal halides or ammonium halides such as potassium bromide, sodium bromide, sodium chloride and ammonium bromide. Further, there are optionally added pH buffers such as borates, oxalates, acetates, carbonates and phosphates, and compounds usually known to be added to a fixer solution such as alkylamines and polyethylene oxides.

The ammonium ion concentration of the fixer solution is generally less than 50 mol%, preferably less than 20 mol% per total ions. More preferably, an ammonium concentration of 0 to 10 mol% prevents stains when a light sensitive material is subjected to a fixing process directly from the bleaching bath, and this reduced ammonium content is also useful for pollution prevention. However, a low ammonium ion concentration occasionally exerts an adverse effect on the fixing capability; therefore, the preferred embodiment of the invention is to jointly use thiocyanates in an amount of 0.5 mol/l to 3.0 mol/l, or to adjust the concentration of thiosulfates to more than 0.4 mol/l, preferably more than 1.0 mol/l and especially 1.2 mol/l to 2.5 mol/l.

Silver may be recovered from the fixer solution by methods known in the art. Useful silver recovery methods are, for example, the electrolysis method described in French Pat. No. 2,299,667; the precipitation method disclosed in Japanese Pat. O.P.I. Pub. No. 73037/1977 and German Pat. No. 2,331,220; the ion exchange method disclosed in Japanese Pat. O.P.I. Pub. No. 17114/1976 and German Pat. 2,548,237; and the metal substitution method described in British Pat. No. 1,353,805.

In view of the rapid processability, it is particularly preferable that an in-line silver recovery from a tanked solution be practiced using electrolysis or an ion exchange resins. Of course, silver recovery from an overflowed waste solution is also applicable.

The replenishing volume of the fixer solution is less than 1,200 ml, preferably 20 ml to 1,000 ml, and especially 50 ml to 800 ml per square meter of a light-sensitive material.

The pH of the fixer solution is preferably in a range from 4 to 8.

The fixer solution may use compounds represented by Formula [FA] set forth on page 56 of the specification of Japanese Pat. Application No. 48931/1988 or exemplified compounds thereof, so that generation of sludge is noticeably reduced even when small batches of light-sensitive materials are processed with the fixer solution over a long period of time.

The compounds represented by Formula [FA] given in the above specification can be synthesized by those general methods which are described in U.S. Pat. Nos. 3,335,161 and 3,260,718. These compounds may be used singly or

in combination. Favorable results are obtained by adding the compounds of Formula [FA] in an amount of 0.1 g to 200 g per liter of the processing solution.

The fixer solution may contain sulfites and sulfite-releasing compounds, such as potassium sulfite, sodium sulfite, ammonium sulfite, ammonium hydrogen sulfite, potassium hydrogensulfite, sodium hydrogen sulfite, potassium metabisulfite, sodium metabisulfite and ammonium metabisulfite. Further, there may also be included compounds represented by Formula [B-1] or [B-2] shown on page 60 of the specification of Japanese Pat. Application No. 48931/1988.

These sulfites and sulfurous-acid-releasing compounds are included in an amount of at least 0.05 mol as sulfurous ions per liter of the fixer solution. This value is desirably in a range from 0.08 mol/l to 0.65 mol/l, more desirably 0.10 mol/l to 0.5 mol/l, and most desirably 0.12 mol/l to 0.40 mol/l.

The processing time in the fixer solution can be arbitrarily selected, but it is generally less than 6 minutes and 30 seconds, preferably in a range from 5 seconds to 4 minutes and 20 seconds, and especially in a range from 10 seconds to 3 minutes and 20 seconds.

According to the invention, it is preferable that the bleaching solution and fixer solution be subjected to forced stirring. This facilitates the effect of the invention and enhances the rapid processability. The term "forced stirring" used here means to conduct a forced stirring using a stirring means, and not a usual diffusive moving of the solution. As means for forced stirring, those described in Japanese Pat. Application No. 48930/1988 and Japanese Pat. O.P.I. Pub. No. 206343/1989 can be used.

In the invention, the cross-over time for a light-sensitive material to transfer between tanks, such as from color developing tank to bleaching tank, is preferably not more than 7 seconds in order to improve bleach fog, which is another effect of the invention. Further, another preferable embodiment of the invention is to use a duckbill valve for minimization of the volume of a processing solution brought in by a light-sensitive material.

After the fixing process used according to the invention, a stabilizing process with a stabilizer solution is preferably carried out.

In the invention, it is particularly preferable that the stabilizer solution contain a chelating agent having a chelate stability constant of 8 or more against ferric ions. The term "chelate stability constant" used here means a constant known by "Stability Constant of Metal-ion Complexes" by L.G. Sillen and A.E. Martell, The Chemical Society, London (1964) and "Organic Sequestering Agents" by S. Chaberek and A.E. Martell, Wiley (1959).

Chelating agents having a chelate stability constant of 8 or more against ferric ions include organic acid chelating agents, organic phosphoric acid chelating agents, inorganic phosphoric acid chelating agents and polyhydroxy compounds.

Examples of the chelating agent having a chelate stability constant of 8 or more against ferric ions are the following compounds, but not limited to them. Namely, ethylenediamine diorthohydroxyphenyl acetic acid, diaminopropane tetracetic acid, nitrilotriacetic acid, hydroxyethylenediamine triacetic acid, dihydroxyethyl glycine, ethylenediamine diacetic acid, ethylenediamine dipropionic acid, iminodiacetic acid, diethylenetriamine pentacetic acid, hydroxyethyliminodiacetic acid, diaminopropanol tetracetic acid, transcyclohexanediamine tetracetic acid, glycoetherdiamine tetracetic acid, ethylenediamine tetrakis(methylene phosphonic acid), nitrilotrimethylene phosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, 1,1-diphosphonoethane-2-carboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxy-1-phosphonopropane-1,2,3-tricarboxylic acid, catechol-3,5-diphosphonic acid, sodium pyrophosphate, sodium tetrapolyphosphate and sodium hexametaphosphate. Among them, diethylenetriamine pentacetic acid, nitrilotriacetic acid, nitrilotrimethylene phosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid are preferred; 1-hydroxyethylidene-1,1-diphosphonic acid is particularly preferred.

The addition amount of the above chelating agent is preferably 0.01 to 50 g, and especially 0.05 to 20 g per liter of the stabilizer solution.

Other compounds which are preferably added to the stabilizer solution are ammonium compounds. These are fed as inorganic ammonium salts such as ammonium hydroxide, ammonium bromide, ammonium carbonate, ammonium chloride, ammonium hypophosphite, ammonium phosphate, ammonium phosphite, ammonium fluoride, acid ammonium fluoride, ammonium fluoroborate, ammonium arsenate, ammonium hydrogen carbonate, ammonium hydrofluoride, ammonium hydrogen sulfate, ammonium sulfate, ammonium iodide, ammonium nitrate, ammonium pentaborate, ammonium acetate, ammonium adipate, ammonium tricarboxylate, ammonium benzoate, ammonium carbamate, ammonium citrate, ammonium diethyldithiocarbamate, ammonium formate, ammonium hydrogen malate, ammonium hydrogen oxalate, ammonium phthalate, ammonium hydrogen tartrate, ammonium thiosulfate, ammonium sulfite, ammonium ethylenediamine tetracetate, ammonium ferric ethylenediamine tetracetate, ammonium lactate, ammonium malate, ammonium maleate, ammonium oxalate, ammonium picrate, ammonium pyrrolidine dithiocarbamate, ammonium salicylate, ammonium succinate, ammonium sulfanilate, ammonium tartarate, ammonium thioglycolate and ammonium 2,4,6-trinitrophenylate. These compounds may be used singly or in combination. The addition amount thereof is preferably in a range of 0.001 to 1.0 mol, especially 0.002 to 2.0 mols per liter of the stabilizer solution.

Further, it is preferable that the stabilizer solution contain sulfites. While said sulfites may be any of those organic and inorganic compounds which release sulfite ions, the preferred are inorganic sulfites. Preferable examples include

sodium sulfite, potassium sulfite, ammonium sulfite, ammonium bisulfite, potassium bisulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite, ammonium metabisulfite and hydrosulfite. These sulfates are added to the stabilizer solution in an amount at least 1×10^{-3} mol/l, and preferably 5×10^{-3} to 10^{-1} mol/l; this exerts a good effect particularly on stain prevention. These may be directly incorporated in the stabilizer solution, but addition to the replenishing stabilizer solution is preferred.

Other known compounds to be added to the stabilizer solution are polyvinylpyrrolidone (PVP K-15, K-30, K-90), organic acid salts (citrates, acetates, succinates, oxalates, benzoates, etc.), pH conditioners (phosphates, borates, hydrochloric acid, sulfuric acid, etc.), fungicides (phenol derivatives, catechol derivatives, imidazole derivatives, triazole derivatives, derivatives, organic halides, fungicides known as slime controlling agents in paper & pulpmaking, etc.), fluorescent brighteners, surfactants, preservatives, and salts of metals such as Bi, Mg, Zn, Ni, Al, Sn, Ti, Zr. These compounds can be arbitrarily used within the limits not to impair the effect of the invention.

In the invention, no washing process is needed after the stabilizing process, but there may be carried out, if necessary, a short-time rinsing or surface cleaning with a small amount of water.

In order to bring out the effect of the invention most effectively, it is preferable that soluble iron ions be present in the stabilizer solution.

The concentration of the soluble iron ions is at least 5×10^{-3} mol/l, preferably in a range from 8×10^{-3} to 150×10^{-3} mol/l and especially from 12×10^{-3} to 100×10^{-3} mol/l. These may be added to the stabilizer solution (tanked solution) by being added to the stabilizer replenishing solution or by being dissolved from a light-sensitive material in the stabilizer solution, or these may be added to the stabilizer solution (tanked solution) by being brought from the preceding bath while adhering to a light-sensitive material under processing.

In the invention, there may be used a stabilizer solution in which calcium ions and magnesium ions were reduced to 5 ppm or less through ion-exchange resin treatment; further, the above fungicide and halogen-ion-releasing compound may be added thereto.

The pH of the stabilizer solution according to the invention is preferably in a range from 5.5 to 10.0; the stabilizer solution may contain any of pH conditioners which are known as an alkali and an acid in the art.

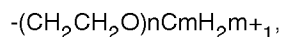
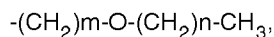
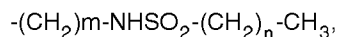
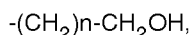
The stabilizing process is carried out in a temperature range of 15 to 70°C, preferably 20 to 55°C. The processing time is less than 120 seconds, preferably 3 to 90 seconds and especially 6 to 50 seconds.

In view of rapid processability and image preservability, it is preferable that replenishment of the stabilizer solution be 0.1 to 50 times and especially 0.5 to 30 times the volume brought from the preceding bath per unit area of a light-sensitive material.

Stabilizing tanks are composed desirably of plural tanks, namely, 2 or more and 6 or less; the more desirable is 2 to 3, and the most desirable is to arrange 2 tanks in counter current mode (the solution is replenished to the subsequent bath and overflowed from the preceding bath).

As color developing agents in the color developing process, aminophenol compounds and p-phenylenediamine compounds are used in general; however, p-phenylenediamine compounds having a water-soluble group are preferred in the invention.

That is, at least one of water-solubilizing groups is present on the amino group or benzene ring of said p-phenylenediamine compound; examples of such a water-solubilizing group are



and

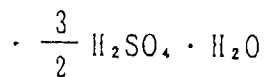
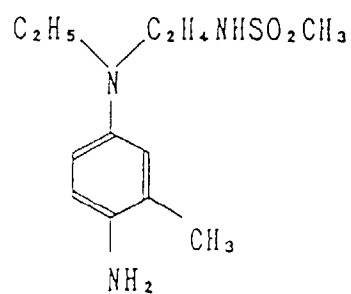


where m and n each represent an integer of 0 or more.

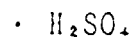
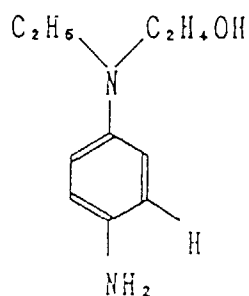
Typical examples of the color developing agent used in the invention are as follows:

[Exemplified color developing agents]

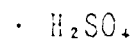
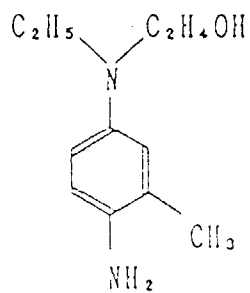
(A - 1)



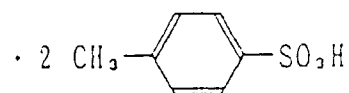
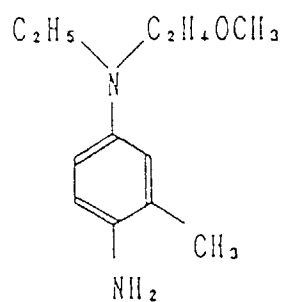
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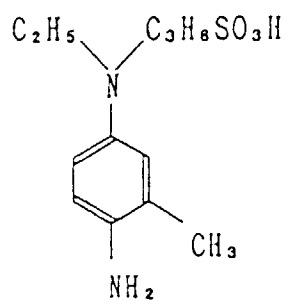
(A - 3)



(A - 4)

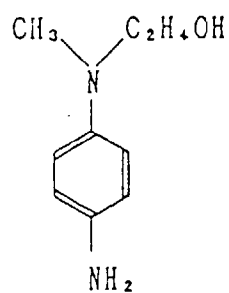


(A - 5)



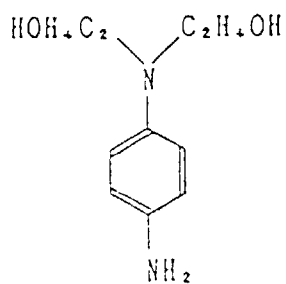
• H₂SO₄

(A - 6)



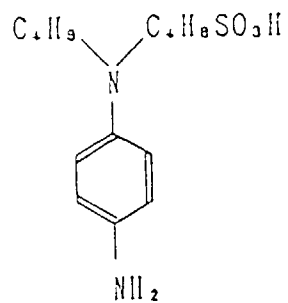
• $\frac{1}{2}$ H₂SO₄

(A - 7)



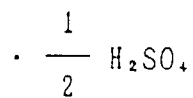
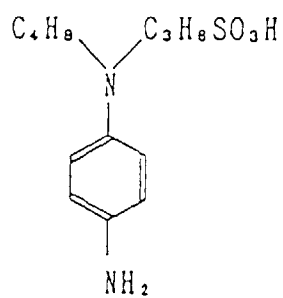
• H₂SO₄

(A - 8)

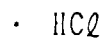
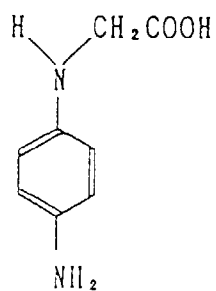


• $\frac{1}{2}$ H₂SO₄

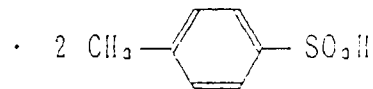
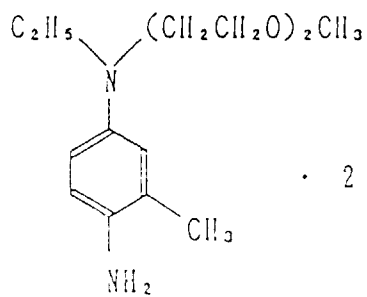
(A - 9)



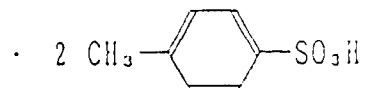
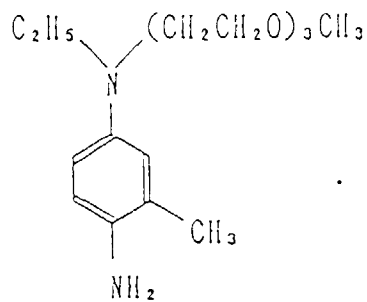
(A - 10)



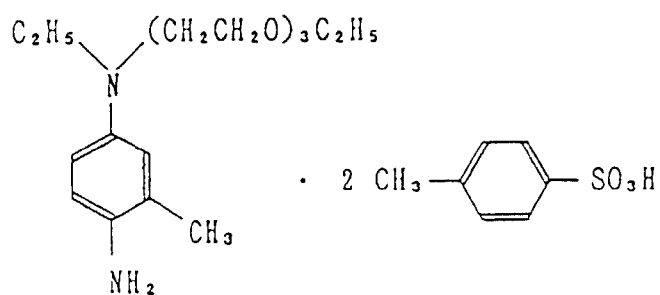
(A - 11)



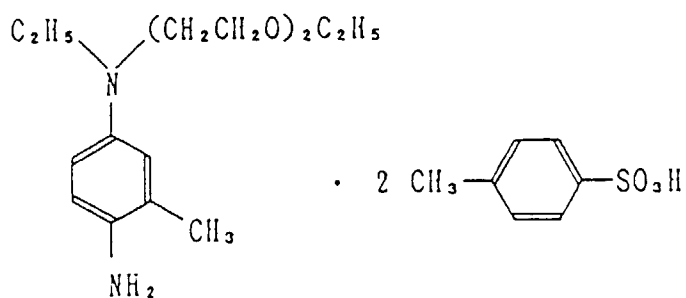
(A - 12)



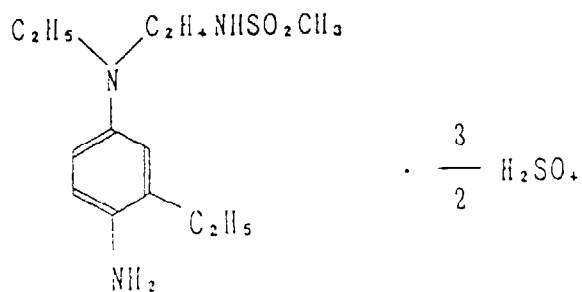
(A - 13)



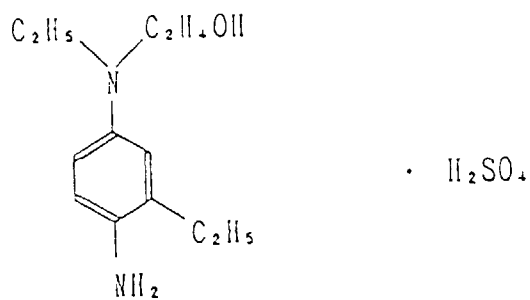
(A - 14)



(A - 15)



(A - 16)



Among the above color developing agents, the preferred for the invention are those denoted by (A-1), (A-2), (A-3), (A-4), (A-6), (A-7) and (A-15), especially (A-1) and (A-3).

These color developing agents are used in the form of salts such as hydrochlorides, sulfates or p-toluenesulfonates. The addition amount thereof is 0.5 mol or more, preferably 1.0×10^{-2} to 1.0×10^{-1} mol and especially 1.5×10^{-2} to 7.0×10^{-2} mol per liter of the color developer solution.

The color developer used in the color developing process may contain conventional alkalis employed in developers, such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, sodium metaborate or borax. Further, there may also be contained other additives, such as benzyl alcohol; alkali metal halides including potassium bromide and potassium chloride; development control agents including citrazinic acid; and preservatives including hydroxylamine, hydroxylamine derivatives (e.g., diethylhydroxylamine), hydrazine derivatives (e.g., hydrazinodiacetic acid) and sulfites.

Moreover, defoamers, surfactants, and organic solvents such as methanol, dimethylformamide or dimethyl sulfoxide may be optionally added thereto.

The pH of the color developer is generally 7 or more, preferably about 9 to 13.

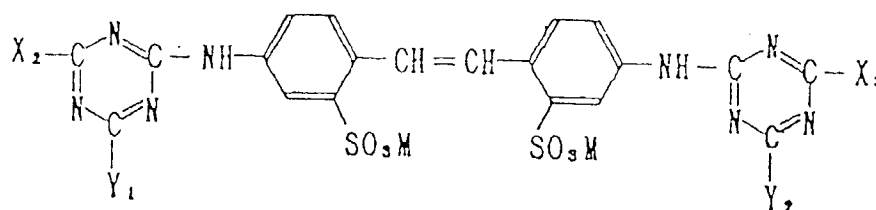
When necessary, the color developer may use, as an antioxidant, tetronic acid, tetronimide, 2-anilinoethanol, dihydroxyacetone, secondary aromatic alcohols, hydroxamic acid, pentose, hexose, or pyrogallol-1,3-dimethylether.

For the purpose of sequestering metal ions, the color developer may use chelating agents selected from aminopolycarboxylic acids such as ethylenediamine tetracetic acid and diethylenetriamine pentacetic acid; organic phosphonic acids such as 1-hydroxyethylidene-1,1-diphosphonic acid; aminopolyposphonic acids such as aminotrimethylenephosphonic acid and ethylenediamine tetraphosphoric acid; oxycarboxylic acids such as citric acid and gluconic acid; phosphonocarboxylic acids such as 2-phosphonobutane-1,2,4-tricarboxylic acid; and polyphosphoric acids such as tripolyphosphoric acid and hexametaphosphoric acid.

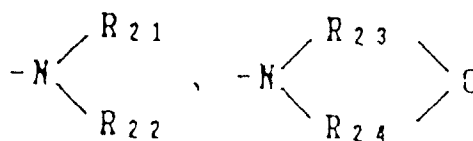
For color negative film, the replenishing volume of the color developer in continuous processing is less than 1,500 ml, preferably 250 ml to 900 ml and especially 300 ml to 700 ml per square meter of a light-sensitive material; for color paper, it is preferably 20 to 300 ml and especially 30 to 160 ml.

To attain the object of the invention the color developer solution used in the invention contains a triazinylstilbene type fluorescent brightener of the following Formula (E):

Formula (E)

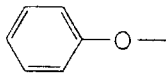
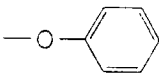
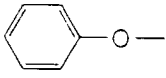
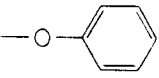
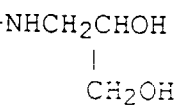
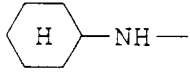
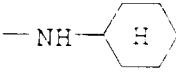
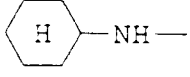
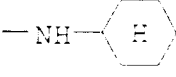
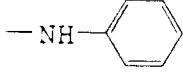
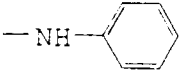
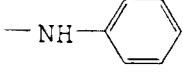
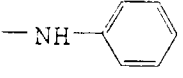
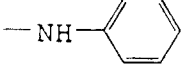
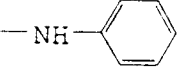
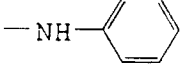
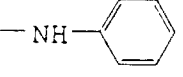


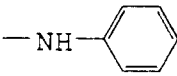
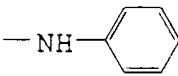
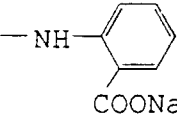
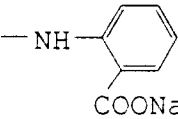
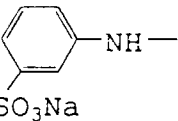
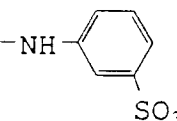
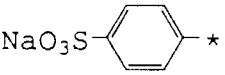
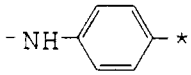
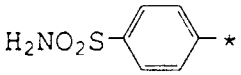
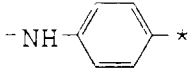
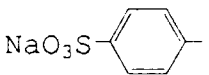
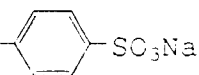
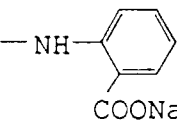
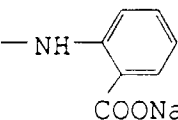
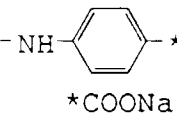
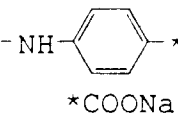
In the above formula, X_2 , X_3 , Y_1 and Y_2 independently represent a hydroxyl group; halogen atom such as chlorine or bromine; alkyl group; aryl group;

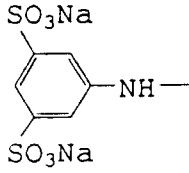
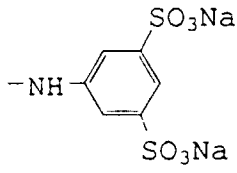
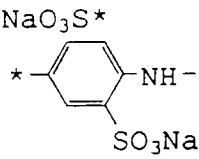
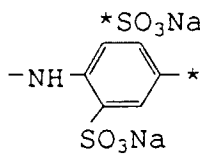
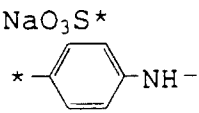
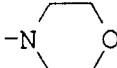
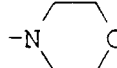
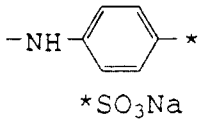
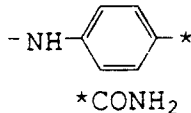
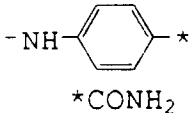
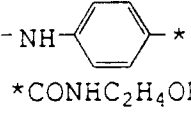
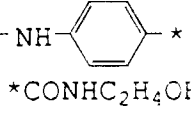
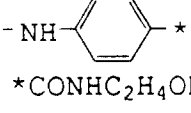
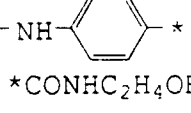
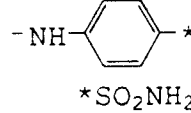
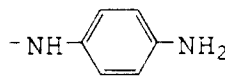
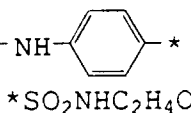
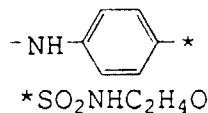


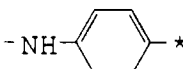
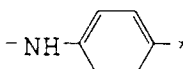
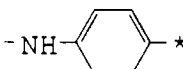
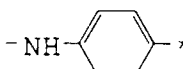
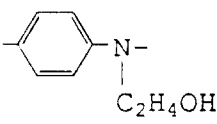
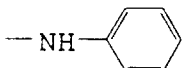
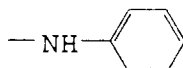
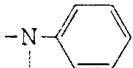
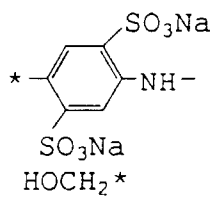
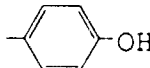
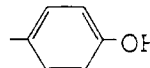
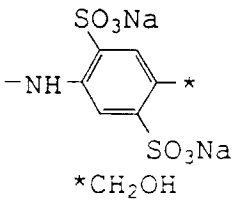
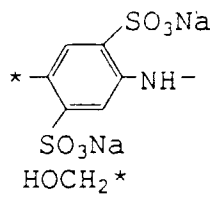
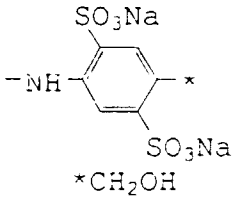
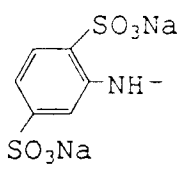
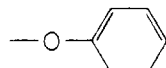
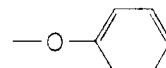
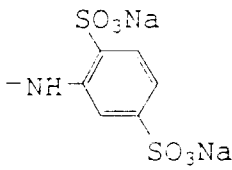
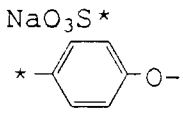
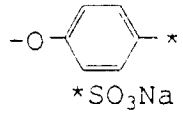
or $-OR_{25}$, where R_{21} and R_{22} independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; R_{23} and R_{24} represent a substituted or unsubstituted alkylene group; R_{25} represents a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; and M represents a cation.

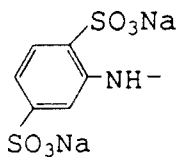
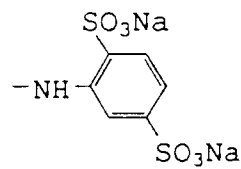
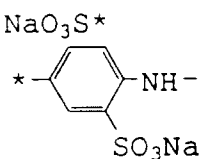
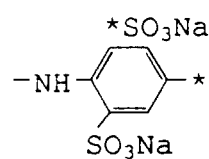
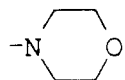
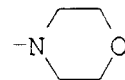
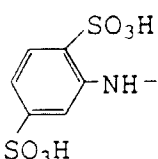
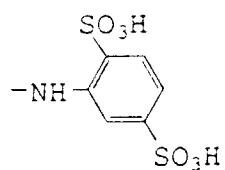
Details of groups and their substituents suitable as compounds of Formula (E) are provided in Japanese Patent Application No. 240400/1990 (page 63 to 64). Examples of the compound represented by Formula (E) are as follows:

Compound	M	X ₂	Y ₁	X ₃	Y ₂
E-1	Na		-NHC ₂ H ₄ OH	-NHC ₂ H ₄ OH	
E-2	Na	HOC ₂ H ₄ NH-	-NHC ₂ H ₄ OH	-NHC ₂ H ₄ OH	-NHC ₂ H ₄ OH
E-3	Na		-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	
E-4	Na	(HOC ₂ H ₄) ₂ N-	-OCH ₃	-OCH ₃	-NHC ₂ H ₄ SO ₃ Na
E-5	Na	HOHCH ₂ CNH-	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	
E-6	Na	(HOC ₂ H ₄) ₂ N-	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂
E-7	Na		-NHC ₂ H ₄ OH	-NHC ₂ H ₄ OH	
E-8	Na		-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	
E-9	Na	HO-			-OH
E-10	Na	H ₂ N-			-NH ₂
E-11	Na	CH ₃ O-			-OCH ₃
E-12	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH

Compound	M	X ₂	Y ₁	X ₃	Y ₂
E-13	Na	-(HOC ₂ H ₄) ₂ N			-N(C ₂ H ₄ OH) ₂
E-14	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH
E-15	Na		-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	
E-16	Na	 *NH-	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	 *-SO ₃ Na
E-17	Na	 *NH-	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	 *-SO ₂ NH ₂
E-18	Na		-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	
E-19	Na	HOH ₂ CHCH ₂ CNH- CH ₃	-CH ₃ O	-CH ₃ O	-NHCH ₂ -CH-* CH ₃ *CH ₂ OH
E-20	Na	(HOC ₂ H ₄) ₂ N-			-N(C ₂ H ₄ OH) ₂
E-21	Na	HOC ₂ H ₄ NH-	 *COONa	 *COONa	-NHC ₂ H ₄ OH

Compound	M	X ₂	Y ₁	X ₃	Y ₂
E-22	Na		-NHC ₂ H ₅	-NHC ₂ H ₅	
E-23	Na		-NHCH ₃	-NHCH ₃	
E-24	Na				
E-25	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH
E-26	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH
E-27	Na	(HOC ₂ H ₄) ₂ N-			-N(C ₂ H ₄ OH) ₂
E-28	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH
E-29	Na	HOC ₂ H ₄ NH-			-NHC ₂ H ₄ OH

Compound	M	X ₂	Y ₁	X ₃	Y ₂
E-30	Na	(HOC ₂ H ₄) ₂ N-	 -NH- 	 -NH- 	-N(C ₂ H ₄ OH) ₂
E-31	Na		-NH- 	-NH- 	-N()C ₂ H ₄ OH
E-32	Na				
E-33	Na		-NHC ₂ H ₅	-NHC ₂ H ₅	
E-34	Na	CH ₃ O-	-NHCH ₂ CH(OH)CH ₃ -NHCH ₂ CH(OH)CH ₃		-OCH ₃
E-35	Na				
E-36	Na		-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	

Compound	M	X ₂	Y ₁	X ₃	Y ₂
E-37	Na		-N(C ₂ H ₅) ₂	-N(C ₂ H ₅) ₂	
E-38	Na		-NHCH ₃	-NHCH ₃	
E-39	Na	CH ₃ O-	-NH-CH(CH ₂ OH)CH ₃ -NH-CH(CH ₂ OH)CH ₃		-OCH ₃
E-40	Na	CH ₃ O-	-N(C ₂ H ₄ OH) ₂	-N(C ₂ H ₄ OH) ₂	-OCH ₃
E-41	Na	CH ₃ O-	-NHC ₂ H ₄ SO ₃ Na	-NHC ₂ H ₄ SO ₃ Na	-OCH ₃
E-42	Na	CH ₃ O-	-NH(C ₂ H ₄ OH)	-NH(C ₂ H ₄ OH)	-OCH ₃
E-43	Na	CH ₃ O-			-OCH ₃
E-44	K	CH ₃ O-	-NHC ₂ H ₄ SO ₃ K	-N(C ₂ H ₄ OH) ₂	-OCH ₃
E-45	H		-N(C ₂ H ₅) ₂	-N(C ₂ H ₅) ₂	

The above exemplified compounds can be synthesized by known methods. Among these compounds, the preferred are E-4, E-10, E-12, E-24, E-34, E-35, E-35, E-37, E-40, E-42, E-43 and E-44. The addition amount of these compounds is preferably 0.2 g to 10 g and especially 0.4 g to 5 g per liter of color developer solution.

Next, explanation will be made of the light-sensitive material to which the processing method of the invention is applied.

As silver halide grains contained in the light-sensitive material, silver halide grains having a silver chloride content of 80 mol% or more are generally used. The content of silver chloride is desirably 90 mol% or more, more desirably 95 mol% or more, and most desirably 99 mol% or more.

Such silver halide emulsion grains may contain, other than silver chloride, silver bromide and/or silver iodide as silver halide components. In this case, the content of silver bromide is generally 20 mol% or less, preferably 10 mol%

or less and especially 3 mol% or less. When silver iodide is present, its content is generally 1 mol% or less, preferably 0.5 mol% or less, and especially is zero. Silver halide grains containing 80 mol% or more of silver chloride are employed at least in one silver halide emulsion layer, preferably in all silver halide emulsion layers.

The crystal form of these silver halide grains may be any of regular crystals, twinned crystals and other crystal forms, and the ratio of (1.0.0) faces to (1.1.1) faces may be arbitrarily selected. The crystal structure thereof may be the same from the inner portion to the outer portion of grains, or may be a layered structure differing in composition between the inner portion and the outer portion of the grains (core/shell structure). Further, these silver halide grains may be grains which form latent images mainly on their surface, or ones which form latent images mainly at their inner portion. Moreover, tabular silver halide grains may also be used (see Japanese Pat. O.P.I. Pub. No. 113934/1983 and Japanese Pat. Application No. 170070/1984) and silver halide grains described in Japanese Pat. O.P.I. Pub. Nos. 26837/1989, 26838/1989 and 77047/1989.

The above silver halide grains may be formed by any of the acid method, neutral method or ammoniacal method. A combination of these methods is also useful. For example, there may be carried out a procedure in which seed grains are formed by the acid method and the resultant seed grains are then grown to a prescribed grain size by the ammoniacal method, which provides a much faster growth speed. In growing silver halide grains, it is preferable to control the pH and pAg in a reaction vessel appropriately, and to add silver ions and halide ions simultaneously in an amount proportional to the growth speed of silver halide grains as described, for example, in Japanese Pat. O.P.I. Pub. No. 48521/1979.

The silver halide emulsion layer of the light-sensitive material to be processed according to the invention contains color couplers, which react with an oxidation product of a color developing agent to form non-diffusive dyes. These color couplers are preferably united into a non-diffusive state in a light-sensitive layer or adjoining thereto.

Thus, the red-sensitive layer can contain, for example, a non-diffusive color coupler capable of forming cyan color images, a phenol or α -naphthol type coupler in general; the green-sensitive layer can contain, for example, at least one non-diffusive color coupler capable of forming magenta color images, a 5-pyrazolone type color coupler and pyrazolotriazole in general; and the blue-sensitive layer can contain, for example, at least one non-diffusive color coupler capable of forming yellow color images, a color coupler having an open-chained ketomethylene group in general. The color coupler may be a six-, four- or two-equivalent coupler. In the invention, a two-equivalent coupler is preferred.

Examples of suitable couplers may be found, for example, in the monograph "Farbkuppler" by W. Pelz on page 111 of Agfa's research paper "Mitteilungen aus den Forschungslaboratorien der Agfa", Leverkusen/München (1961), vol. III; "The Chemistry of Synthetic Dyes" by K. Venkataraman, Academic Press, vol. 4, pp. 341-387; "The Theory of the Photographic Process", 4th ed., pp. 353-362; and Research Disclosure No. 17643, sec. VII.

In view of the object of the invention, it is particularly preferable to use magenta couplers represented by Formula [M-I] shown on page 26 of the specification of Japanese Pat. O.P.I. Pub. No. 106655/1988 (typical examples thereof are those denoted by Nos. 1 to 77 on pages 29-34 of the same specification); cyan couplers represented by Formula [C-II] or [C-III] shown on page 34 of the same specification (typical examples thereof are those denoted by (C'-1) to (C'-82) and (C"-1) to (C"-36) on pages 37-42 of this specification); and high-speed yellow couplers described on page 20 of the specification (typical examples thereof are those denoted by (Y'-1) to (Y'-39) on pages 21-26 of the specification).

Use of a nitrogen-containing heterocyclic mercapto compound in a light-sensitive material is one of the preferable embodiments of the invention, because it minimizes an adverse effect on photographic properties exerted when some bleaching or fixing solution gets mixed in the developer solution.

Examples of such nitrogen-containing heterocyclic mercapto compounds are those denoted by (I'-1) to (I'-87) on pages 42-45 of the specification of Japanese Pat. O.P.I. Pub. No. 106655/1988.

The silver halide emulsion used in the present invention can be chemically sensitized. Use of sulfur-containing compounds, such as allylisocyanate, allylthiourea and thiosulfate is particularly preferred. Reducing agents can also be used as chemical sensitizers; examples thereof are silver compounds described in Belgian Pat. Nos. 493,464, 568,687; polyamines such as diethylenetriamine according to Belgian Pat. No. 547,323; and aminomethylsulfine derivatives. Further, noble metals and salts thereof, such as gold, platinum, palladium, iridium, ruthenium and rhodium, are also useful sensitizers. This chemical sensitizing method is described on pages 65-72 of R. Kosiovsky's paper in "Zeitschrift für Wissenschaftliche Photographie", vol. 46 (1951); see also the above Research Disclosure No. 17643, sec. III.

The silver halide emulsion can be spectrally sensitized by conventional methods with ordinary polymethine dyes such as neutrocyanine, basic or acidic carboxycyanine, rhodacyanine, hemicyanine; styryl dyes; and oxonol and analogues thereof. The spectral sensitization is described in the monograph "The Cyanine Dyes and Related Compounds" 1964, by F.M. Hamer; "Ullmanns Enzyklopadie der technischen Chemie", 4th ed., vol. 18, p. 431; and Research Disclosure No. 17643, sec. IV.

The silver halide emulsion may use conventional antifoggants and stabilizers. Azaindenes are suitable stabilizers; tetra- and penta-azaindene are preferred, and those substituted with a hydroxyl or amino group are particularly preferred. Compounds of this type are shown, for example, in Birr's paper in "Zeitschrift für Wissenschaftliche Photogra-

phie", vol.47 (1952), pp. 2-58; and Research Disclosure No. 17643, sec. IV.

The components of the light-sensitive material can be contained by conventional methods; refer to U.S. Pat. Nos. 2,322,027, 2,533,514, 3,689,271, 3,764,336 and 3,765,897. Some of the components - for example, couplers and UV absorbers - can be contained in the form of charged latex as described in German Offenlegungsschrift 2,541,274 and European Pat. Application 14,921. Also, some of the components can be fixed as a polymer in a light-sensitive material as seen, for example, in German Offenlegungsschrift 2,044,992 and U.S. Pat. Nos. 3,370,952 and 4,080,211.

As supports of the light-sensitive material, conventional supports may be used. For example, color paper may use reflective supports such as paper supports, which may be coated with polyolefin such as polyethylene or polypropylene; see Research Disclosure No. 17643sec. V and VI.

The method of the invention can be applied to any of coupler-containing light-sensitive materials to be processed by the so-called internal development, such as color paper, color negative film, color positive film, color reversal film for slides, color reversal film for movies, color reversal film for TV and reversal color paper.

EXAMPLES

The present invention is hereunder described in more detail with the examples. Comparative Examples 1 to 5 are included to demonstrate the effects of certain of the features of the invention.

Comparative Example 1

Multilayered silver halide color photographic light-sensitive material (1) was prepared by coating the layers having the following compositions on the titanium-oxide-containing polyethylene side of a paper support coated with titanium-oxide-containing polyethylene. The coating solutions were prepared as follows:

Coating solution for 1st layer

There were dissolved 26.7 g of yellow coupler (Y-1), 10.0 g of dye image stabilizer (ST-1), 6.67 g of dye image stabilizer (ST-2) and 0.67 g of additive (HQ-1) in a mixture of 6.67 g of high boiling solvent (DNP) and 60 ml of ethyl-acetate. Then, the solution was dispersed, with an ultrasonic homogenizer, in 220 ml of a 10% gelatin aqueous solution containing 7 ml of a 20% solution of surfactant (SU-1) to prepare a yellow coupler dispersion. The dispersion was mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared under the conditions described later.

Coating solutions for 2nd to 7th layers were prepared in the same manner as with the coating solution for 1st layer.

As hardeners, (H-1) was added in 2nd and 4th layers, and (H-2) in 7th layer. As coating aids, (SU-2) and (SU-3) were added to adjust surface tension.

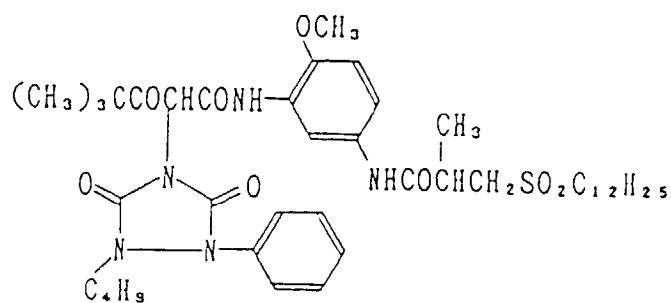
Layer	Composition Addition amount (g/m ²)	
7th layer (protective layer)	gelatin	1.0
6th layer (UV absorbing layer)	gelatin	0.4
	UV absorbent (UV-1)	0.10
	UV absorbent (UV-2)	0.04
	UV absorbent (UV-3)	0.16
	antistain agent (HQ-1)	0.01
	DNP	0.2
	PVP	0.03
	anti-irradiation dye (AI-2)	0.02

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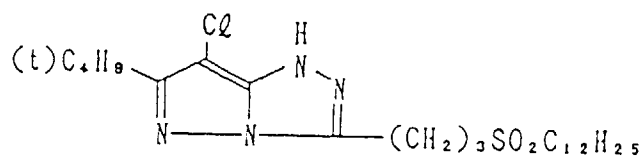
(continued)

Layer	Composition Addition amount (g/m ²)
5th layer (red-sensitive layer)	gelatin 1.30
	red-sensitive silver chlorobromide emulsion (Em-R) in terms of Ag 0.21
	cyan coupler (C-1) 0.17
	cyan coupler (C-2) 0.25
	dye image stabilizer (ST-1) 0.20
	antistain agent (HQ-1) 0.01
	HBS-1 0.20
	DOP 0.20
4th layer (UV absorbing layer)	gelatin 0.94
	UV absorbent (UV-1) 0.28
	UV absorbent (UV-2) 0.09
	UV absorbent (UV-3) 0.38
	antistain agent (HQ-1) 0.03
	DNP 0.40
3rd layer (green-sensitive layer)	gelatin 1.40
	green-sensitive silver chlorobromide emulsion (Em-G) in Ag 0.17
	magenta coupler (M-1) 0.35
	dye image stabilizer (ST-3) 0.15
	dye image stabilizer (ST-4) 0.15
	dye image stabilizer (ST-5) 0.15
	DNP 0.20
	anti-irradiation dye (AI-1) 0.01
2nd layer (intermediate layer)	gelatin 1.20
	antistain agent (HQ-2) 0.12
	DIDP 0.15
1st layer (blue-sensitive layer)	gelatin 1.20
	blue-sensitive silver chlorobromide emulsion (Em-B) in Ag 0.26
	yellow coupler (Y-1) 0.80
	dye image stabilizer (ST-1) 0.30
	dye image stabilizer (ST-2) 0.20
	anti-irradiation agent (HQ-1) 0.02
	anti-irradiation dye (AI-3) 0.01
	DNP 0.20
Support	polyethylene-laminated paper

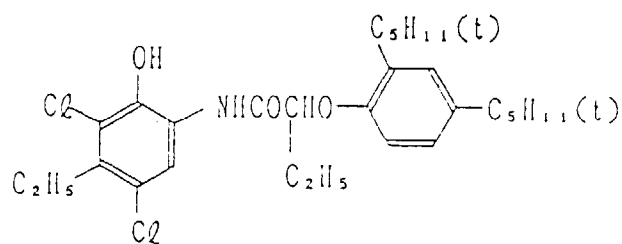
Y - 1



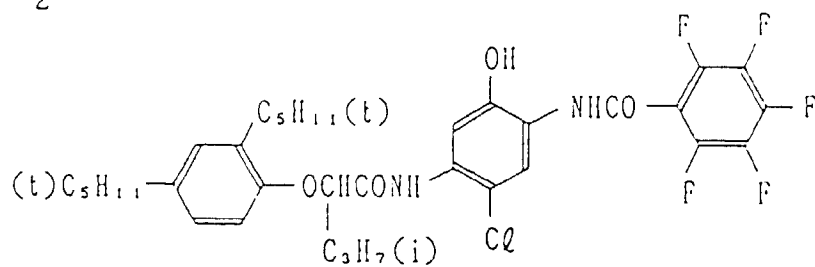
M - 1



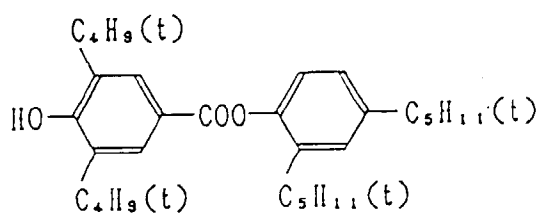
C - 1



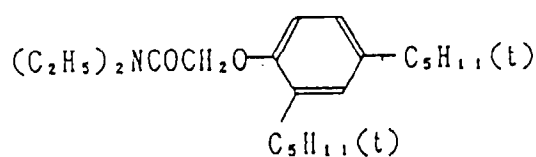
C - 2



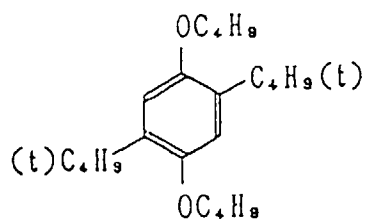
ST - 1



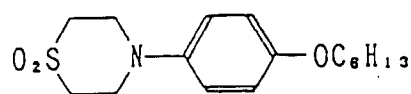
ST - 2



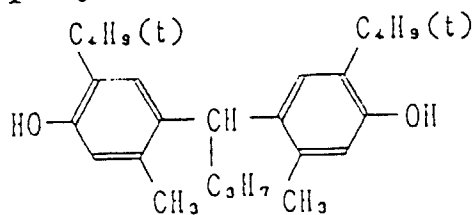
ST - 3



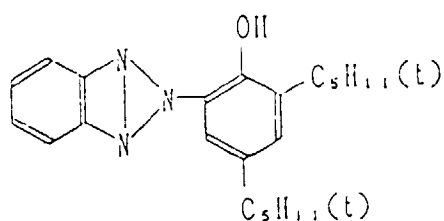
ST - 4



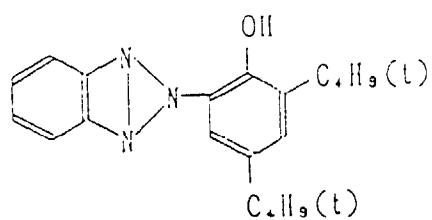
ST - 5



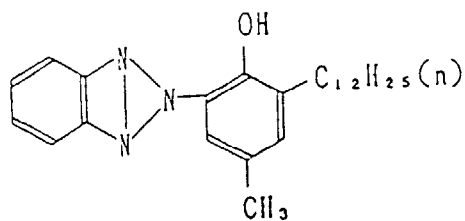
UV - 1



UV - 2



UV - 3



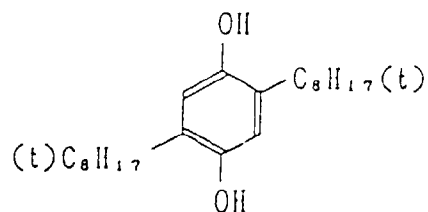
DOP: dioctyl phthalate

DNP: dinonyl phthalate

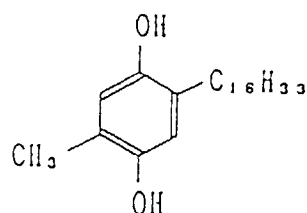
DIDP: diisodecyl phthalate

PVP: polyvinyl pyrrolidone

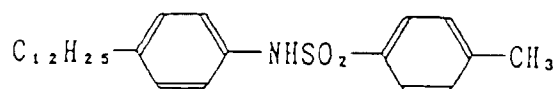
HQ - 1



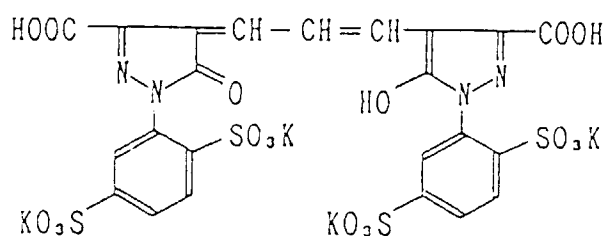
HQ - 2



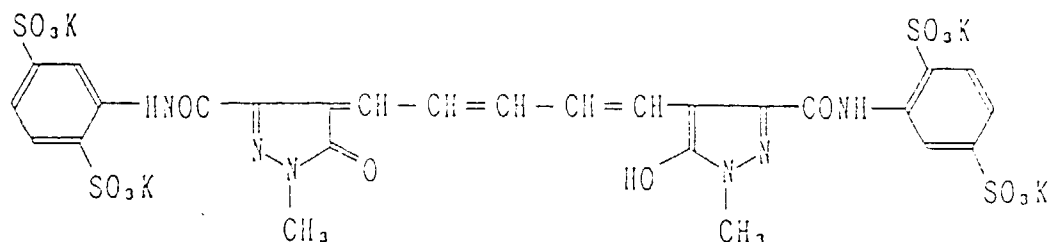
HBS - 1



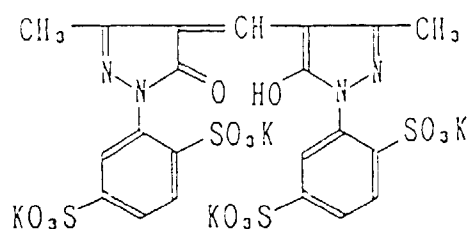
AI - 1



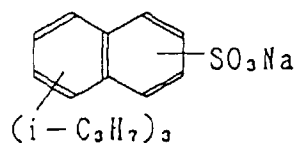
AI - 2



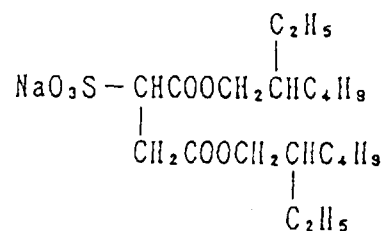
AI - 3



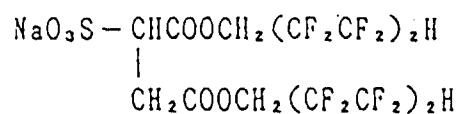
S U - 1



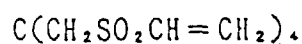
S U - 2



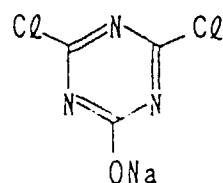
S U - 3



H - 1



H - 2



[Preparation of blue-sensitive silver halide emulsion]

The following (solution A) and (solution B) were simultaneously added to 1,000 ml of a 2% gelatin aqueous solution at 40°C over a period of 30 minutes, while controlling pAg at 6.5 and pH at 3.0. Then, the following (solution C) and (solution D) were simultaneously added thereto over a period of 180 minutes, while controlling pAg at 7.3 and pH at 5.5. During the addition, control of the pAg was made according to the method described in Japanese Pat. O.P.I. Pub. No. 45437/1984, and the pH was controlled with aqueous solution of sulfuric acid or sodium hydroxide.

(solution A)	
Sodium chloride	3.42 g
Potassium chloride	0.03 g
water was added to make	200 ml

(solution B)	
Sodium nitrate	10 g
Water was added to make	200 ml

(solution C)	
Sodium chloride	102.7 g
Potassium bromide	1.0 g
Water was added to make	600 ml

(solution D)	
Silver nitrate	300 g
Water was added to make	600 ml

After completing the addition, desalination was conducted using a 5% aqueous solution of Demol N made by Kao Atlas and a 20% aqueous solution of magnesium sulfate, and the emulsion obtained was mixed with an aqueous solution of gelatin. Monodispersed cubic emulsion EMP-1 thus obtained had an average grain size of 0.85 μm , variation coefficient (σ/r) of 0.07 and silver chloride content of 99.5 mol%.

Emulsion EMP-1 was then subjected to chemical sensitization for 90 minutes at 50°C using the following compounds, so that a blue-sensitive silver halide emulsion(Em-B) was prepared.

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX
Stabilizer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizing dye (BS-1)	4×10^{-4} mol/mol AgX
Sensitizing dye (BS-2)	1×10^{-4} mol/mol AgX

[Preparation of green-sensitive silver halide emulsion]

Monodispersed cubic emulsion EMP-2 having an average grain size of 0.43 μm , variation coefficient (σ/r) of 0.08 and silver chloride content of 99.5 mol% was prepared in the same manner as with EMP-1, except that the addition times of (solution A) & (solution B) and that of (solution C) & (solution D) were changed.

Then, EMP-2 was subjected to chemical sensitization for 120 minutes at 55°C using the following compounds to obtain a green-sensitive silver halide emulsion (Em-G).

Sodium thiosulfate	1.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Stabilizer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizing dye (GS-1)	4×10^{-4} mol/mol AgX

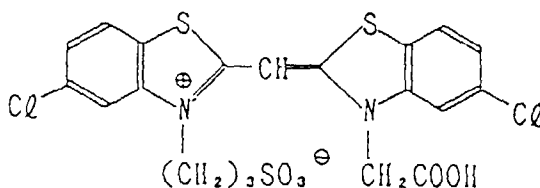
[Preparation of red-sensitive silver halide emulsion]

Monodispersed cubic emulsion EMP-3 having an average grain size of 0.50 μm , variation coefficient (σ/r) of 0.08 and silver chloride content of 99.5 mol% was prepared in the same manner as with EMP-1, except that the addition times of (solution A) & (solution B) and that of (solution C) & (solution D) were changed.

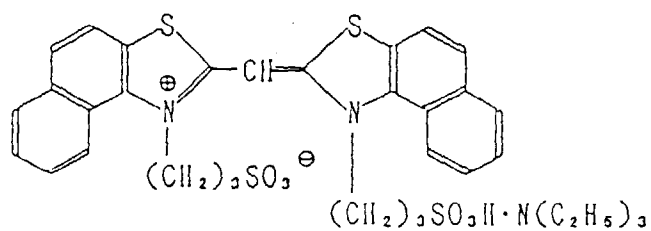
Then, EMP-3 was subjected to chemical sensitization for 90 minutes at 60°C using the following compounds to obtain a red-sensitive silver halide emulsion (Em-R).

Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Stabilizer (STAB-1)	6×10^{-4} mol/mol AgX
Sensitizing dye (RS-1)	1×10^{-4} mol/mol AgX

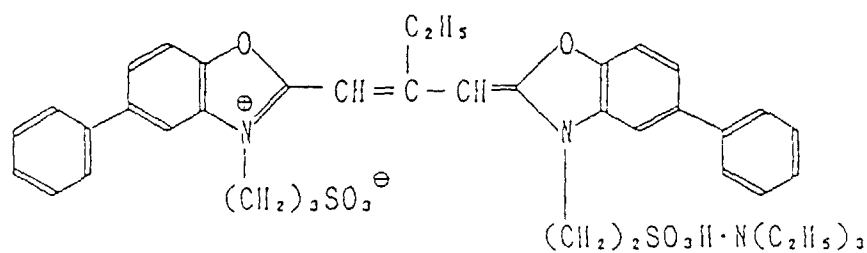
BS - 1



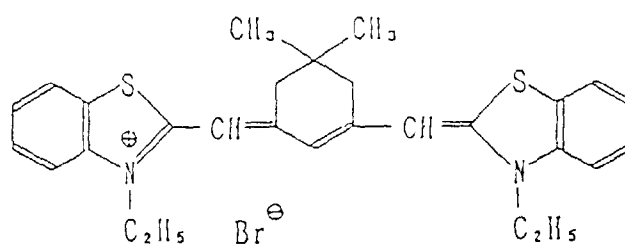
BS - 2



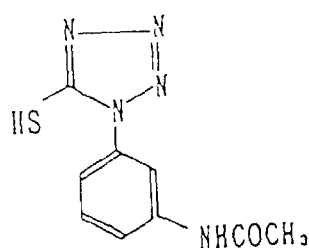
GS - 1



RS - 1



STAB - 1



Samples prepared as above were subjected to conventional wedge exposure and then to a running treatment according to the following process (1):

Process (1)	Temperature	Time	Replenished volume
	(°C)	(sec)	(ml/m ²)
Color developing	38	20	61
Bleaching	38	20	30
Fixing	38	20	30

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(continued)

Process (1)	Temperature	Time	Replenished volume
	(°C)	(sec)	(ml/m ²)
Stabilizing	30	1st tank: 20 2nd tank: 20	101
Drying	60 to 80	30	

Notes*: The 1st and 2nd tanks of the stabilizing bath were arranged in a counter current mode, and replenishment was made to the 2nd tank.

Compositions of the processing solutions were as follows:

(Color developer tank solution)	
Diethylene glycol	15 g
Potassium bromide	0.01 g
Potassium chloride	2.3 g
Potassium sulfite (50% solution)	0.5 ml
Color developing agent [3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate]	6 g
Diethylhydroxylamine (85%)	5 g
Triethanol amine	10 g
Potassium carbonate	30 g
Ethylenediamine tetracetic acid	2 g
Fluorescent brightener (PK-Conc., product of Nisso)	2 g

Water was added to make the total volume 1 liter, and pH was adjusted to 10.15 with potassium hydroxide or sulfuric acid.

(Color developer replenishing solution)	
Diethylene glycol	17 g
Potassium chloride	3 g
Potassium sulfite (50% solution)	1.0 ml
Color developing agent [3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate]	8.8 g
Diethylhydroxylamine (85%)	7 g
Triethanol amine	10 g
Potassium carbonate	30 g
Ethylenediamine tetracetic acid	2 g
Fluorescent brightener (PK-Conc., product of Nisso)	2.5 g

Water was added to make the total volume 1 liter, and pH was adjusted to 11.0 with potassium hydroxide or sulfuric acid.

(Bleaching tank solution)	
Organic acid ferric complex salt (see Table 1)	
Ethylenediamine tetracetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water was added to 1 liter, and pH was adjusted to a value shown in Table 1 with aqueous ammonia or glacial acetic acid.

(Bleaching replenisher)	
Organic acid ferric complex salt (see Table 1, the addition amount was increased by 20%)	

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(continued)

(Bleaching replenisher)	
Ethylenediamine tetracetate	2 g
Ammonium bromide	178 g
Glacial acetic acid	50 ml

Water was added to 1 liter, and pH was adjusted to a value shown in Table 1 with aqueous ammonia or glacial acetic acid.

(Fixer tank solution and fixer replenishing solution)	
Ammonium thiosulfate	180 g
Ammonium thiocyanate	120 g
Sodium metabisulfite	3 g
Ethylenediamine tetracetic acid	0.8 g

Water was added to make 1 liter, and pH was adjusted to pH 6.5 with acetic acid and aqueous ammonia.

(Stabilizer tank solution and stabilizer replenishing solution)	
Orthophenylphenol	0.15 g
ZnSO ₄ ·7H ₂ O	0.2 g
Ammonium sulfite (40% solution)	5.0 ml
1-hydroxyethylidene-1,1-diphosphonic acid (60% solution)	2.5 g
Ethylenediamine tetracetic acid	2.0 g
Fluorescent brightener (Cinoparl SFP, product of Ciba-Geigy)	2.0 g

The pH was adjusted to 7.8 with aqueous ammonia or sulfuric acid, and water was added to make 1 liter.

The light-sensitive material sample was subjected to running treatment by being processed in an automatic processing machine filled with the above tank solutions of color developer, bleacher, fixer and stabilizer, while the replenishing solutions of color developer, bleacher, fixer and stabilizer were fed through a measuring pump at 3-minute intervals. This running treatment was carried on till the replenished volume came to twice the volume of the tank solution.

After the running treatment, the reflected yellow density of an unexposed portion of the processed wedge was measured. The amount of residual silver in an exposed portion was also measured by the X-ray fluorometry. Further, the processing solutions of experiment Nos. (1-1), (1-2), (1-3), (1-4), (1-5), (1-6), (1-23), (1-24), (1-25), (1-26) and (1-27) were preserved at 38°C after completion of the running treatment and then checked for generation of tar (tarring).

Next, samples were processed by the following process(2) instead of process (1) and evaluated likewise.

Process (2)	Temperature	Time	Replenished volume
	(°C)	(sec)	(ml/m ²)
Color developing	38	20	61
Bleach-fixing	38	40	90
Stabilizing	30	1st tank: 20 2nd tank: 20	101
Dyeing	60 to 80		30

(Bleach-fixer tank solution and replenishing solution)	
Organic acid sodium ferric salt (see Table 1)	
Ethylenediamine tetracetic acid	3 g
Ammonium thiosulfate (70% solution)	123 g
Ammonium sulfite (40% solution)	51 g

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The pH was adjusted as shown in Table 1 with aqueous ammonia or sulfuric acid, and water was added to make 1 liter.

Experiments 1-24, 1-25 and 1-26 (see Table 1 below) were processed according to process (2) to provide a comparison with process (1).

5

10

15

20

25

30

35

40

45

50

55

Table 1

Experiment No.	Organic acid iron complex salt		pH	Process	Yellow density of unexposed portion	Residual silver amount of exposed portion (mg/100 cm ²)	Tarring
	Compound	Addition amount (mol/l)					
1-1	EDTA·Fe	0.30	4.5	(1)	0.08	0.8	A
1-2	NTA·Fe	0.30	4.5	(1)	0.07	1.4	A
1-3	CyDTA·Fe	0.30	4.5	(1)	0.07	0.9	A
1-4	EDTMP·Fe	0.30	4.5	(1)	0.08	0.8	A
1-5	NTMP·Fe	0.30	4.5	(1)	0.08	0.8	A
1-6	(A-1)·Fe	0.30	4.5	(1)	0.08	0.0	A
1-7	(A-4)·Fe	0.30	4.5	(1)	0.08	0.0	
1-8	(A-7)·Fe	0.30	4.5	(1)	0.09	0.0	
1-9	(A-9)·Fe	0.30	4.5	(1)	0.07	0.0	
1-10	(A-1)·Fe	0.05	4.5	(1)	0.06	0.4	
1-11	(A-1)·Fe	0.10	4.5	(1)	0.09	0.2	
1-12	(A-1)·Fe	0.19	4.5	(1)	0.09	0.1	
1-13	(A-1)·Fe	0.23	4.5	(1)	0.09	0.0	
1-14	(A-1)·Fe	0.40	4.5	(1)	0.10	0.0	
1-15	(A-1)·Fe	0.50	4.5	(1)	0.10	0.0	
1-16	(A-1)·Fe	0.60	4.5	(1)	0.11	0.0	
1-17	(A-1)·Fe	0.30	1.5	(1)	0.06	0.2	
1-18	(A-1)·Fe	0.30	2.0	(1)	0.06	0.1	
1-19	(A-1)·Fe	0.30	3.0	(1)	0.06	0.0	
1-20	(A-1)·Fe	0.30	4.0	(1)	0.07	0.0	
1-21	(A-1)·Fe	0.30	5.0	(1)	0.07	0.0	
1-22	(A-1)·Fe	0.30	5.5	(1)	0.09	0.1	
1-23	(A-1)·Fe	0.30	6.0	(1)	0.12	0.2	B
1-24	DTPA·Fe	0.30	4.5	(2)	0.12	0.2	B
1-25	(A-1)·Fe	0.30	4.5	(2)	0.20	more than 0.3 mg	C
1-26	DTPA·Fe/ CyDTA·Fe/ (A-1)·Fe (B-1)·Fe	0.1/0.1/0.1 0.30	4.5	(2)	0.15	1.0 mg	C
1-27			4.5	(1)	0.08	0.0	A

In the table, the meanings of the respective abbreviations are; EDTA·Fe: sodium iron (III) ethylenediamine tetracetate, NTA·Fe: sodium iron (III) nitrilotriacetate, CyDTA·Fe: sodium iron (III), 2-cyclohexanediamine tetracetate, EDTMP·Fe: sodium iron (III) ethylenediaminetetramethylene phosphonate, NTMP·Fe: sodium iron (III) nitrilotrimeth-

ylene phosphonate, DTPA-Fe: sodium iron (III) diethylenetriamine pentacetate, and (A-1)-Fe: sodium iron (III) salt of (A-1).

The rating of tar generation is;

- 5 A: no tar
 B: slight tar
 C: tar is obviously observed
 D: heavy tar

10 It is seen from Table 1 that the effect of the invention is favorably brought about when a light-sensitive material having a silver chloride content of 80 mol% or more is processed in a bleacher solution containing a specific organic acid ferric complex salt. Further, it is understood, from experiment Nos. 1-15 to 1-21 and 1-6, that the effect of the invention is favorably exerted when the addition amount of the organic acid ferric complex salt of the compound according to the invention is 0.1 mol/l or more and preferably 0.2 to 1.5 mol/l; from experiment Nos. 1-17 to 1-23 and 1-6, that a bleach solution pH of not more than 5.5, particularly 2.5 to 5.5, yields good results, and from experiment Nos. 1-24 to 1-26 and 1-6, that the effect of the invention is obviously demonstrated when process (1) is used.

Comparative Example 2

20 A multilayered color photographic light-sensitive material sample was prepared by forming the following layers in sequence on a triacetylcellulose film support.

	(Light-sensitive material)	Addition amount
25	1st layer: antihalation layer	
	Black colloidal silica	0.2
	UV absorbent (UV-1)	0.23
	High boiling solvent (Oil-1)	0.18
30	Gelatin	1.4
	2nd layer: 1st intermediate layer	
	Gelatin	1.3
	3rd layer: low-speed red-sensitive layer	
35	Silver iodobromide emulsion (average grain size: 0.4 μ m, AgI: 2.0 mol%)	1.0
	Sensitizing dye (SD-1)	1.8×10^{-5} mol/molAg
	Sensitizing dye (SD-2)	2.8×10^{-4} mol/molAg
	Sensitizing dye (SD-3)	3.0×10^{-4} mol/molAg
40	Cyan coupler (C-1)	0.70
	Colored cyan coupler (CC-1)	0.066
	DIR compound (D-1)	0.03
	DIR compound (D-3)	0.01
	High boiling solvent (Oil-1)	0.64
45	Gelatin	1.2
	4th layer: medium-speed red-sensitive layer	
	Silver iodobromide emulsion (average grain size: 0.7 μ m, AgI: 8.0 mol%)	0.8
50	Sensitizing dye (SD-1)	2.1×10^{-5} mol/molAg
	Sensitizing dye (SD-2)	1.9×10^{-4} mol/molAg
	Sensitizing dye (SD-3)	1.9×10^{-4} mol/molAg
	Cyan coupler (C-1)	0.28
	Colored cyan coupler (CC-1)	0.027
55	DIR compound (D-1)	0.01
	High boiling solvent (Oil-1)	0.26
	Gelatin	0.6

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(continued)

	(Light-sensitive material)	Addition amount
5	5th layer: high-speed red-sensitive layer	
	Silver iodobromide emulsion (average grain size: 0.8 μm , Agl: 8.0 mol%)	1.7
	Sensitizing dye (SD-1)	1.9×10^{-5} mol/molAg
	Sensitizing dye (SD-2)	1.7×10^{-4} mol/molAg
10	Sensitizing dye (SD-3)	1.7×10^{-4} mol/molAg
	Cyan coupler (C-1)	0.05
	Cyan coupler (C-2)	0.10
	Colored cyan coupler (CC-1)	0.02
	DIR compound (D-1)	0.025
15	High boiling solvent (Oil-1)	0.17
	Gelatin	1.2
	6th layer: 2nd intermediate layer	
	Gelatin	0.8
20	7th layer: low-speed green-sensitive layer	
	Silver iodobromide emulsion (average grain size: 0.4 μm , Agl: 2.0 mol%)	1.1
	Sensitizing dye (SD-4)	6.8×10^{-5} mol/molAg
	Sensitizing dye (SD-5)	6.2×10^{-4} mol/molAg
25	Magenta coupler (M-1)	0.54
	Magenta coupler (M-2)	0.19
	Colored magenta coupler (CM-1)	0.06
	DIR compound (D-2)	0.017
	DIR compound (D-3)	0.01
30	High boiling solvent (Oil-2)	0.81
	Gelatin	1.8
	8th layer: medium-speed green-sensitive layer	
35	Silver iodobromide emulsion (average grain size: 0.7 μm , Agl: 8.0 mol%)	0.7
	Sensitizing dye (SD-6)	1.9×10^{-4} mol/molAg
	Sensitizing dye (SD-7)	1.2×10^{-4} mol/molAg
	Sensitizing dye (SD-8)	1.5×10^{-5} mol/molAg
	Magenta coupler (M-1)	0.07
40	Magenta coupler (M-2)	0.03
	Colored magenta coupler (CM-1)	0.04
	DIR compound (D-2)	0.018
	High boiling solvent (Oil-2)	0.30
45	Gelatin	0.8
	9th layer: high-speed green-sensitive layer	
	Silver iodobromide emulsion (average grain size: 1.0 μm , Agl: 8.0 mol%)	1.7
	Sensitizing dye (SD-6)	1.2×10^{-4} mol/molAg
50	Sensitizing dye (SD-7)	1.0×10^{-4} mol/molAg
	Sensitizing dye (SD-8)	3.4×10^{-6} mol/molAg
	Magenta coupler (M-1)	0.09
	Magenta coupler (M-3)	0.04
	Colored magenta coupler (CM-1)	0.04
55	High boiling solvent (Oil-2)	0.31
	Gelatin	1.2

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(continued)

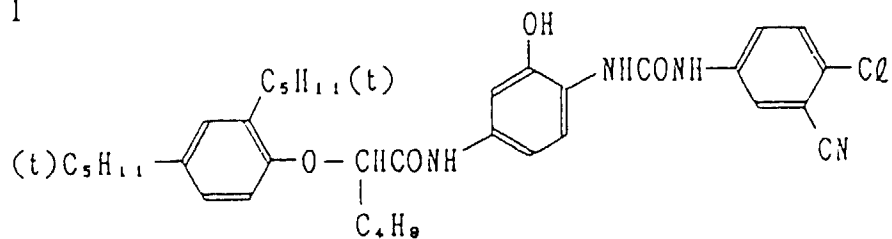
	(Light-sensitive material)	Addition amount
5	10th layer: yellow filter layer	
	Yellow colloidal silver	0.05
	Antistain agent (SC-1)	0.1
	High boiling solvent (Oil-2)	0.13
	Gelatin	0.7
10	Formalin scavenger (HS-1)	0.09
	Formalin scavenger (HS-2)	0.07
	11th layer: low-speed blue-sensitive layer	
15	Silver iodobromide emulsion (average grain size: 0.4 μm , Agl: 2.0 mol%)	0.5
	Silver iodobromide emulsion (average grain size: 0.7 μm , Agl: 8.0 mol%)	
	Sensitizing dye (SD-9)	5.2×10^{-4} mol/molAg
	Sensitizing dye (SD-10)	1.9×10^{-5} mol/molAg
	Yellow coupler (Y-1)	0.65
20	Yellow coupler (Y-2)	0.24
	DIR compound (D-1)	0.03
	High boiling solvent (Oil-2)	0.18
	Gelatin	1.3
	Formalin scavenger (HS-1)	0.08
25	12th layer: high-speed blue-sensitive layer	
	Silver iodobromide emulsion (average grain size: 1.0 μm , Agl: 8.0 mol%)	1.0
	Sensitizing dye (SD-9)	1.8×10^{-4} mol/molAg
	Sensitizing dye (SD-10)	7.9×10^{-5} mol/molAg
30	Yellow coupler (Y-1)	0.15
	Yellow coupler (Y-2)	0.05
	High boiling solvent (Oil-2)	0.074
	Gelatin	1.30
35	Formalin scavenger (HS-1)	0.05
	Formalin scavenger (HS-2)	0.12
	13th layer: 1st protective layer	
40	Fine grain silver iodobromide emulsion (average grain size: 0.08 μm , Agl: 1 mol%)	0.4
	UV absorbent (UV-1)	0.07
	UV absorbent (UV-2)	0.10
	High boiling solvent (Oil-1)	0.07
	High boiling solvent (Oil-3)	0.07
	Formalin scavenger (HS-1)	0.13
45	Formalin scavenger (HS-2)	0.37
	Gelatin	1.3
	14th layer: 2nd protective layer	
50	Alkali-soluble matting agent (average particle size: 2 μm)	0.13
	Polymethylmethacrylate (average particle size: 3 μm)	0.02
	Slipping agent (WAX-1)	0.04
55	Gelatin	0.6

Besides the above compounds, there were used coating aid Su-1, dispersing aid Su-2, viscosity controller, hardeners H-1 and H-2, stabilizer ST-1 and antifoggants AF-1 (Mw: 10,000) and AF-2 (Mw: 1,100,000).

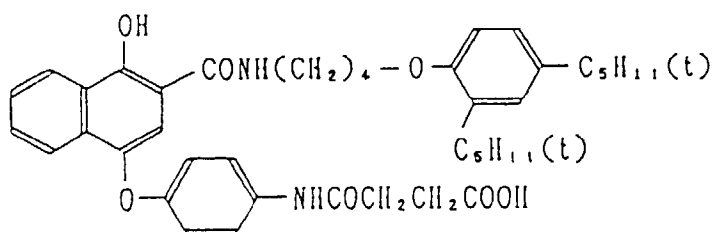
The emulsions used in the above sample were prepared utilizing the procedure of Comparative Example 1. Each

emulsion was optimally subjected to gold-sulfur sensitization. The average grain sizes used above are grain sizes of cubes converted from actual shapes.

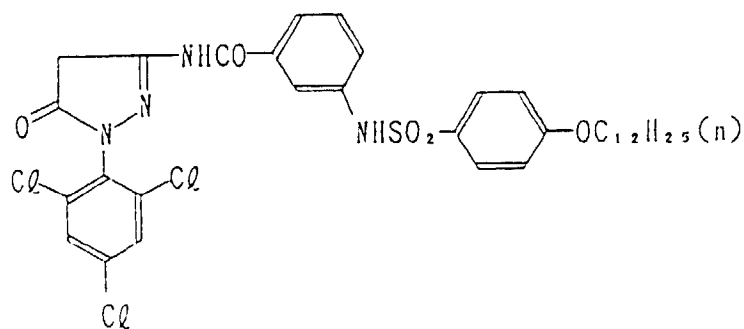
C - 1



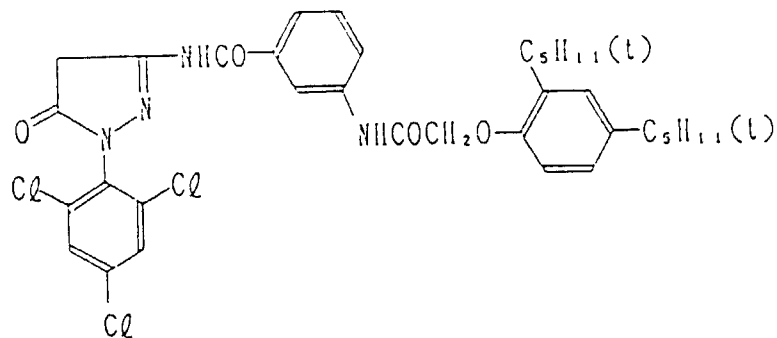
C - 2



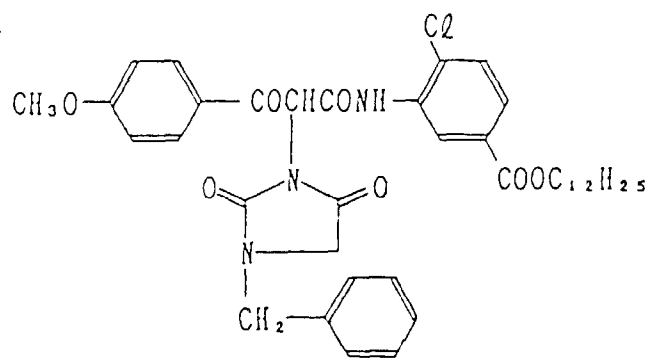
M - 1



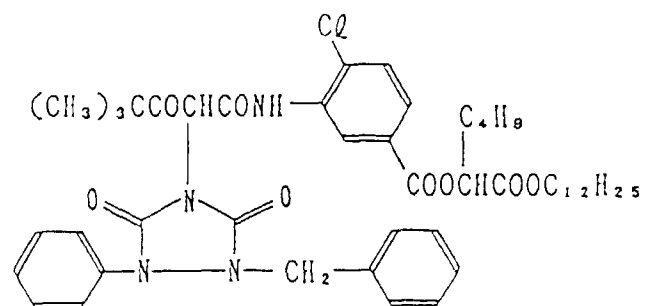
M - 2



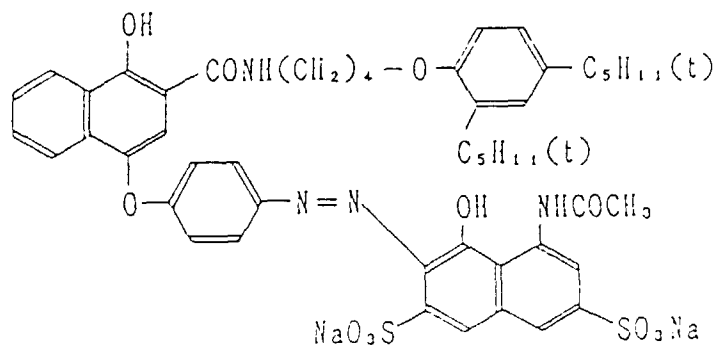
Y - 1



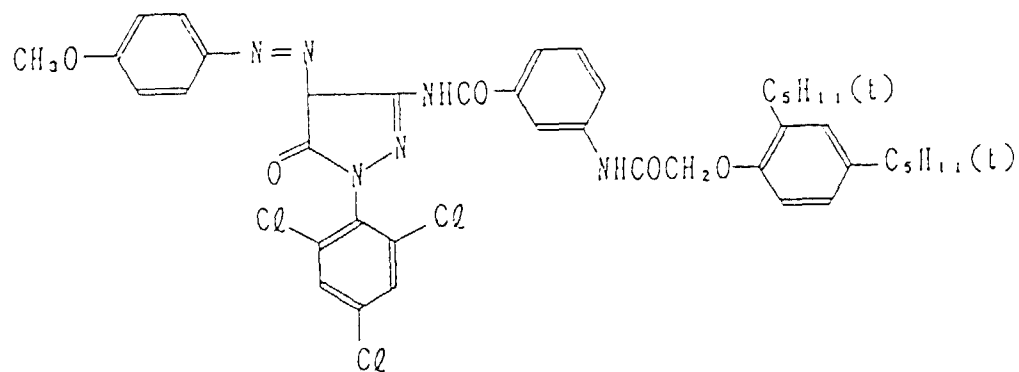
Y - 2



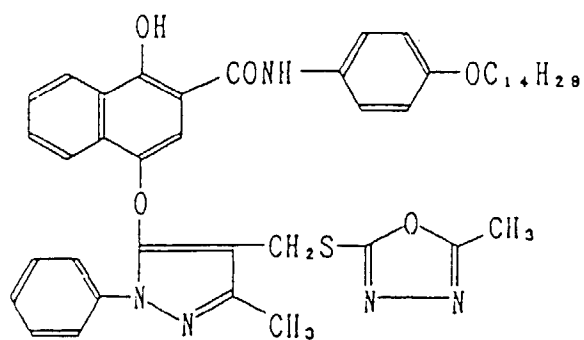
CC - 1



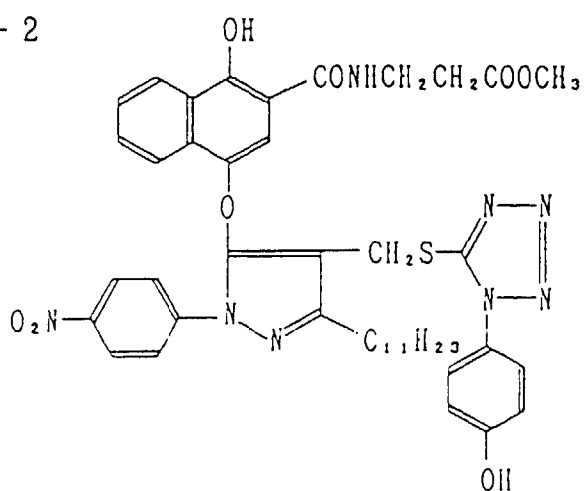
CM - 1



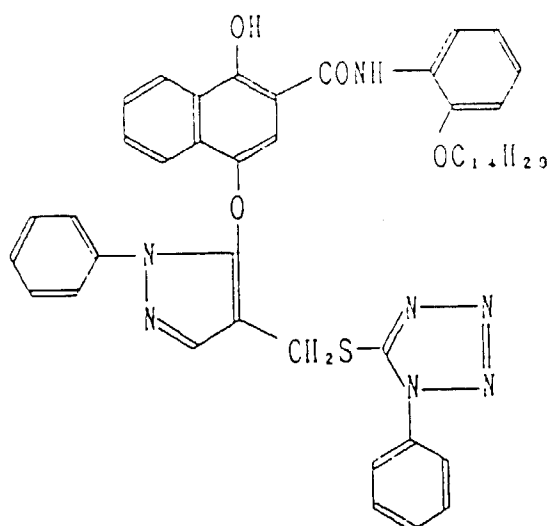
D - 1



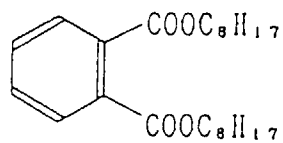
D - 2



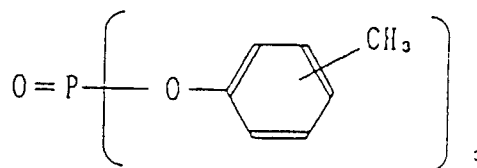
D - 3



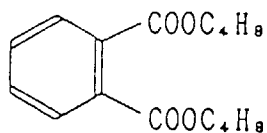
Oil-1



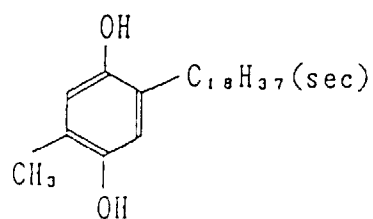
Oil-2



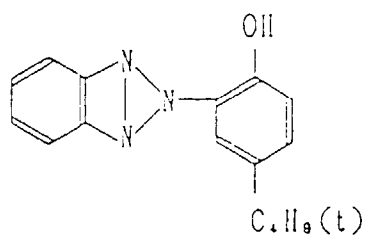
Oil-3



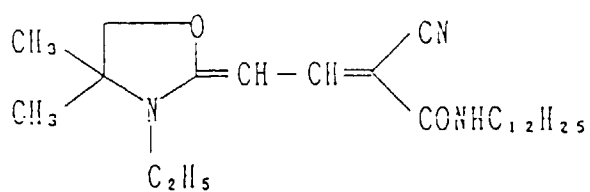
SC-1



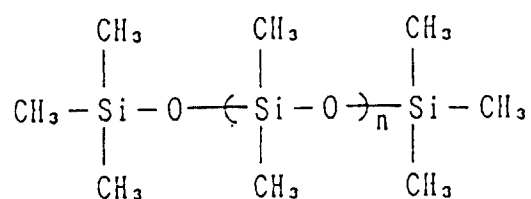
UV-1



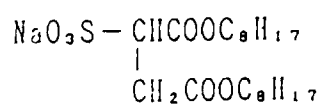
UV-2



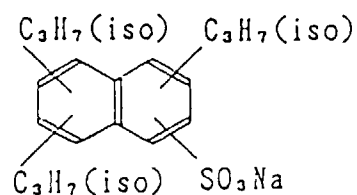
W A X - 1

weight-average molecular weight $M_w = 3,000$

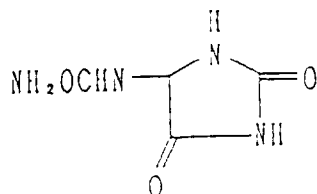
S u - 1



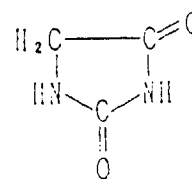
S u - 2



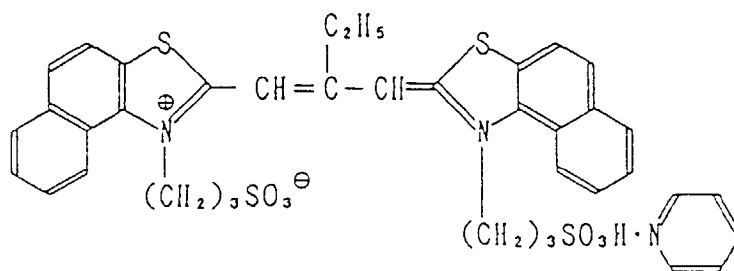
H S - 1



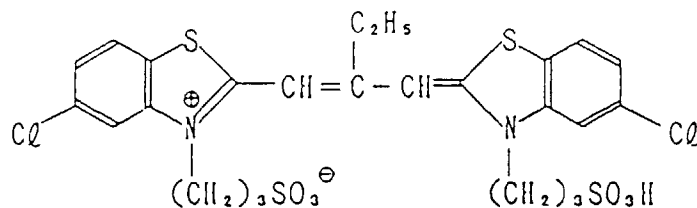
H S - 2



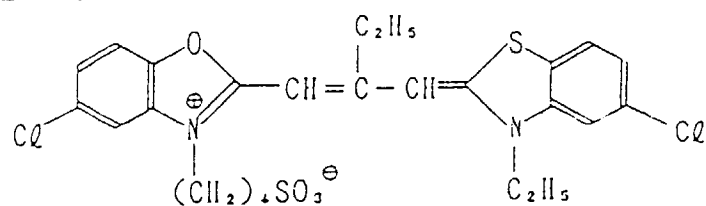
S D - 1



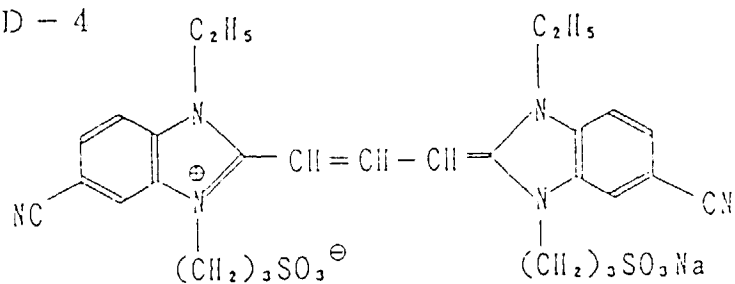
S D - 2



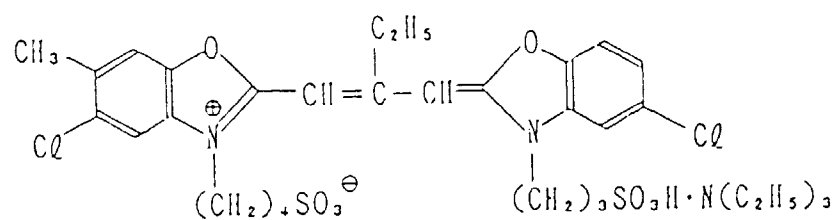
SD - 3



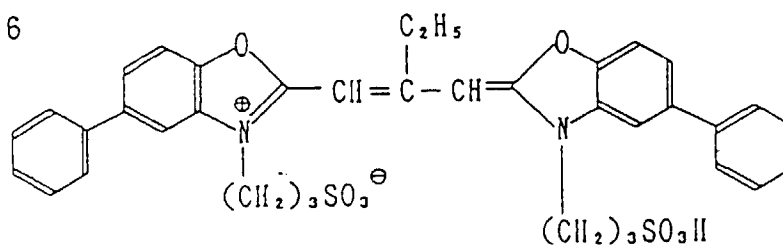
SD - 4



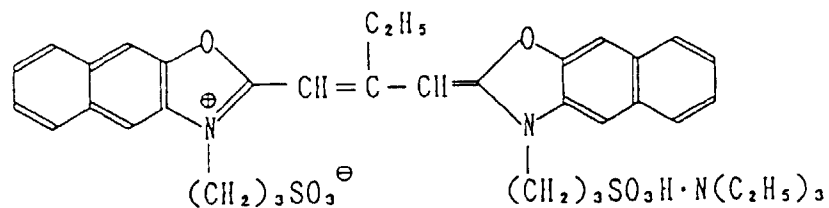
SD - 5



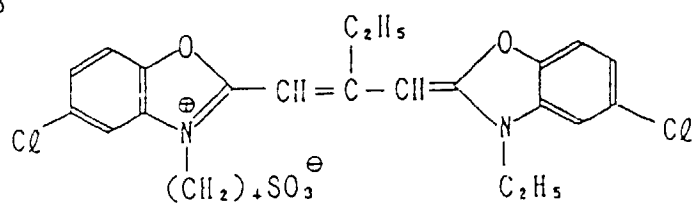
SD - 6



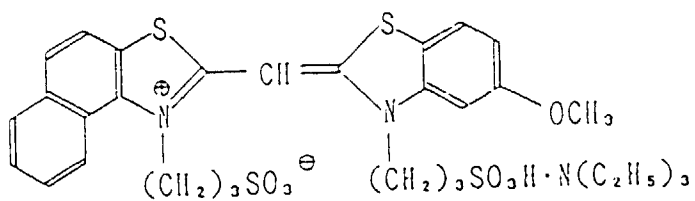
SD - 7



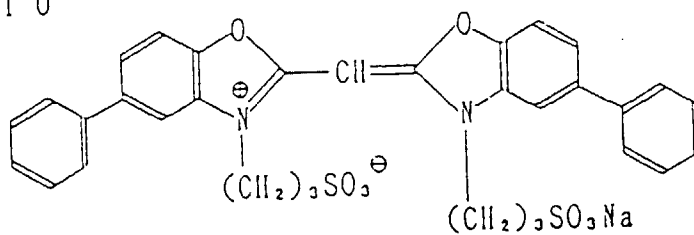
SD - 8



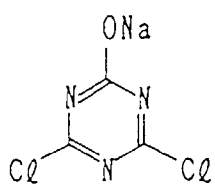
SD - 9



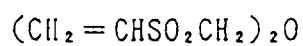
SD - 10



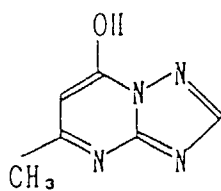
H - 1



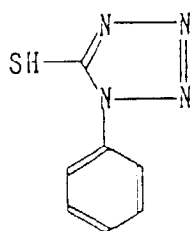
H - 2



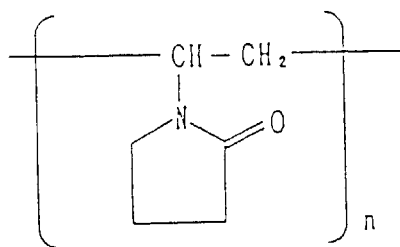
ST - 1



A F - 1



A F - 2



n : degree of polymerization

The samples prepared as above were wedge-exposed to a white light and then processed under the following conditions:

Process A	Processing time	Processing temperature	Replenished volume*
Color developing	3 min 15 sec	38°C	536 ml
Bleaching	45 sec	38°C	134 ml
Fixing	1 min 30 sec	38°C	536 ml
Stabilizing**	90 sec	38°C	536 ml
Drying	1 min	40 to 70°C	

Notes*: Replenished volumes are values per square meter of a light-sensitive material.

** : The 1st and 2nd tanks of the stabilizing bath were arranged in a counter current mode, and replenishment was made to the 2nd tank.

Compositions of the processing solutions used in the above processes are as follows:

(Color developer solution)	
Potassium carbonate	30 g
Sodium hydrogencarbonate	2.5 g
Potassium sulfite	3.0 g
Sodium bromide	1.3 g
Potassium iodide	1.2mg
Hydroxylamine sulfate	2.5 g
Sodium chloride	0.6 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.5 g
Diethylenetriamine pentacetic acid	3.0 g
Potassium hydroxide	1.2 g

Water was added to make 1 liter, and pH was adjusted to 10.06 with potassium hydroxide or a 20% sulfuric acid.

(Color developer replenishing solution)	
Potassium carbonate	35 g
Sodium hydrogencarbonate	3 g
Potassium sulfite	5 g
Sodium bromide	0.4 g
Hydroxylamine sulfate	3.1 g
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	5.8 g
Potassium hydroxide	2 g
Diethylenetriamine pentacetic acid	3.0 g

Water was added to make 1 liter, and the pH was adjusted to 10.12 with potassium hydroxide or a 20% sulfuric acid solution.

The bleacher tank solution, fixer tank solution, stabilizer tank solution and respective replenishing solutions were the same as those used in Comparative Example 1.

In parallel with the above process A, the color paper prepared and wedge-exposed in Comparative Example 1 was processed using the processing solutions employed in Comparative Example 1 under conditions of experiment No. 1-6. This is referred to as process B.

<Experiment 2-1>

Process A (color negative film)

(color developer) - (bleacher) - (fixer) - (stabilizer)

Process B (color paper)

(color developer) - (bleacher) - (fixer) - (stabilizer)

A parallel running treatment illustrated above was conducted by replenishing the processing solutions in respective processing baths. In this running treatment, all the bleacher solution overflowed in process A was used as a replenishing solution in process B.

That is, the piping was arranged in advance so as to flow (replenish) all the overflowed bleacher solution for color negative film to the bleaching bath for color papers. The running treatment was continued till the replenished volume of the bleacher solution came to twice the volume of the bleacher tank solution for color papers (this is called 2 rounds and abbreviated to 2R). In this parallel running treatment, the processing rate of color paper and that of color negative film were kept at a constant ratio, at which 24 sheets of B-sized color paper (8.2 cm x 11.7 cm) were processed while 1 roll of color negative film (135 size, 24 exposures) was processed.

<Experiment 2-2>

The color paper was running-treated only by process B. This running treatment was conducted in 2 rounds (2 R) as with experiment 2-1. Replenishment of the bleacher solution was made at a rate of 20 ml/m².

<Experiments 2-3 to 2-6>

Running treatments were conducted in the same manner as in experiment 2-1, except that types of oxidizing agents were changed as shown in Table 2. The color paper was evaluated in the same manner as in Comparative Example 1, at the start and after completion (after 2 R) of the running treatment. Further, the processing solutions after the running treatment were preserved at 38°C and then checked for generation of tar.

Table 2

Experi- ment No.	Organic acid iron complex salt		pH	Yellow density of unexposed portion		Residual silver amount of exposed portion (mg/100 cm ²)		Tarring	Remarks
	Compound	Addition amount (mol/l)		At the start	After comple- tion	At the start	After comple- tion		
2-1	(A-1)·Fe	0.30	4.5	0.08	0.06	0.0	0.0	A	Invention
2-2	(A-1)·Fe	0.30	4.5	0.08	0.08	0.0	0.0	A	Invention
2-3	EDTA·Fe	0.30	4.5	0.08	0.10	0.8	1.0	B	Comparison
2-4	EDTMP·Fe	0.30	4.5	0.08	0.10	0.7	0.9	C	Comparison
2-5	(B-1)·Fe	0.30	4.5	0.08	0.06	0.0	0.0	A	Invention
2-6	(A-1)·Fe/ (A-1)·Fe	0.15/ 0.15	4.5	0.08	0.08	0.0	0.0	A	Invention

Comparative Example 3

Using the color paper and processing solutions prepared in Comparative Example 1, a running treatment was

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conducted according to process (1), while varying the replenishing volume of the bleacher solution as shown in Table 3 below. This running treatment was carried out till the replenished volume of the bleacher solution came to twice the volume of the bleacher tank solution for color paper.

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Table 3

Experi- ment No.	Organic acid iron complex salt		pH	Yellow density of unexposed portion		Residual silver amount of exposed portion (mg/100 cm ²)		Tarr- ing	Replen- ished volume (ml/cm ²)	Remarks
	Compound	Addition amount (mol/l)		At the start	After comple- tion	At the start	After comple- tion			
3-1	EDTA·Fe	0.30	4.5	0.07	0.08	0.8	0.8	A	60	Comp.
3-2	EDTA·Fe	0.30	4.5	0.07	0.08	0.8	0.8	A	50	Comp.
3-3	EDTA·Fe	0.30	4.5	0.07	0.16	0.8	1.8	C	30	Comp.
3-4	EDTA·Fe	0.30	4.5	0.07	0.25	0.8	2.6	D	10	Comp.
3-5	CyDTA·Fe	0.30	4.5	0.07	0.13	0.8	1.2	B	30	Comp.
3-6	(A-1)·Fe	0.30	4.5	0.08	0.07	0.0	0.0	A	60	Inv.
3-7	(A-1)·Fe	0.30	4.5	0.08	0.08	0.0	0.0	A	50	Inv.
3-8	(A-1)·Fe	0.30	4.5	0.08	0.08	0.0	0.0	A	30	Inv.
3-9	(A-1)·Fe	0.30	4.5	0.08	0.09	0.0	0.1	A - B	10	Inv.
3-10	(B-1)·Fe	0.30	4.5	0.08	0.07	0.0	0.0	A	30	Inv.
3-11	(A-1)·Fe/ (B-1)·Fe	0.15/ 0.15	4.5	0.08	0.08	0.0	0.0	A	30	Inv.

Comp.: Comparison Inv.: Invention

Comparative Example 4

Samples were prepared by varying coating weights of silver in the color paper prepared in Comparative Example 1 as shown in Table 4, while adjusting coating weights of couplers so as to make gradations after wedge exposure and processing approximate to one another. These samples were evaluated in the same manner as in Comparative Example 1 [process (1) was employed].

Table 4

No.	Coating weight of silver (mg/100 m ²)
4-1	8.5
4-2	7.5
4-3	6.5
4-4	5.5

It was found from the evaluation results that when the coating weight of silver was less than 7.5 mg/100 cm², the effect of the invention was noticeable, particularly, desilverizing capability was greatly improved.

Comparative Example 5

After subjecting the color paper prepared in Comparative Example 1 to wedge exposure, time step experiments of the bleacher were made with processing solutions which had undergone the running treatment. The results are shown in Table 5.

Table 5

Experiment No.	Organic acid iron complex salt		pH	60"		40"		30"		25"		20"	
	Compound	Addition amount (mol/l)		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
5-1	EDTA·Fe	0.30	4.5	0.06	0.1	0.07	0.1	0.08	0.3	0.08	0.8	0.18	1.9
5-2	CyDTA·Fe	0.30	4.5	0.06	0.0	0.07	0.1	0.08	0.4	0.07	0.9	0.21	1.8
5-3	(A-1)·Fe	0.30	4.5	0.06	0.0	0.07	0.0	0.08	0.0	0.08	0.0	0.08	0.1
5-4	(B-1)·Fe	0.30	4.5	0.06	0.0	0.07	0.0	0.08	0.0	0.07	0.0	0.08	0.1
5-5	(A-1)·Fe/ (B-1)·Fe	0.15/ 0.15	4.5	0.06	0.0	0.07	0.0	0.07	0.0	0.07	0.1	0.08	0.1

Notes (1) Yellow density of unexposed portion

(2) Residual silver amount of exposed portion (mg/100 cm²)

Example 6

The paper prepared in Comparative Example 1 was exposed through an optical wedge and then subjected to a

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running treatment in the same manner as in experiment No. 1-6 of Comparative Example 1, except that the following solution was used as a developer.

(Color developer tank solution)	
Diethylene glycol	15 g
Potassium bromide	0.01 g
Potassium chloride	2.3 g
Potassium sulfite (50% solution)	6.5 ml
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	6 g
Diethylhydroxylamine (85%)	5 g
Triethanol amine	10 g
Potassium carbonate	30 g
Ethylenediamine tetracetic acid	2 g
Fluorescent brightening agent (see Table 6)	2 g

Water was added to make the total volume 1 liter, and then the pH was adjusted to 10.15 with potassium hydroxide or sulfuric acid.

(Color developer replenishing solution)	
Diethylene glycol	17 g
Potassium chloride	3 g
Potassium sulfite (50% solution)	1.0 ml
Color developing agent (3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate)	8.8 g
Diethylhydroxylamine (85%)	7 g
Triethanol amine	10 g
Potassium carbonate	30 g
Ethylenediamine tetracetic acid	2 g
Fluorescent brightening agent (see Table 6)	2.5 g

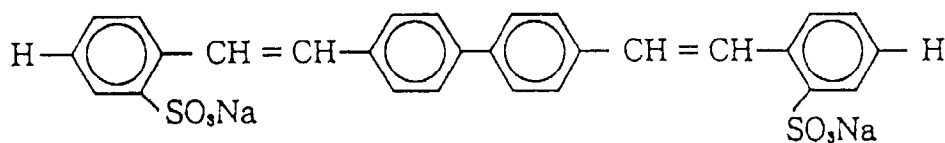
Water was added to make the total volume 1 liter, and then the pH was adjusted to 11.0 with potassium hydroxide or sulfuric acid.

The sample was evaluated in the same manner as in Comparative Example 1, the results are shown in Table 6.

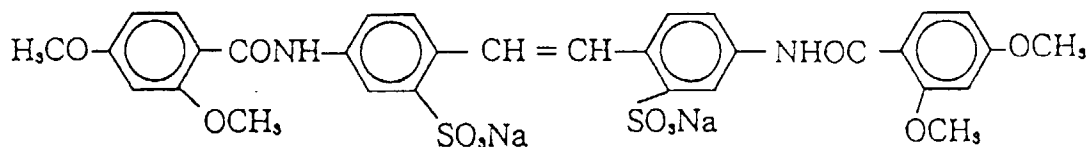
Table 6

Experiment No.	Brightener	Yellow density in unexposed portion	Amount of residual silver in exposed portion	Tarring
6-1	E-34	0.08	0.0	A
6-2	not added	0.10	0.0	A to B
6-3	①	0.09	0.1	A to B
6-4	②	0.09	0.0	B
6-5	③	0.09	0.1	A to B

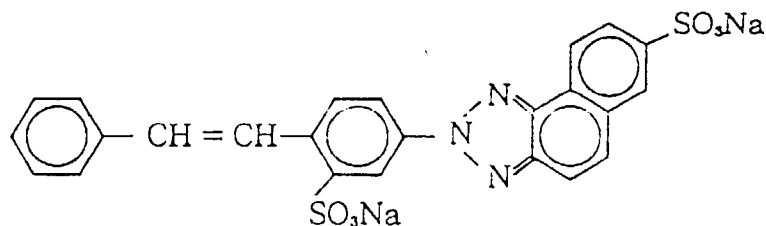
Brightener ①



Brightener ②



Brightener ③

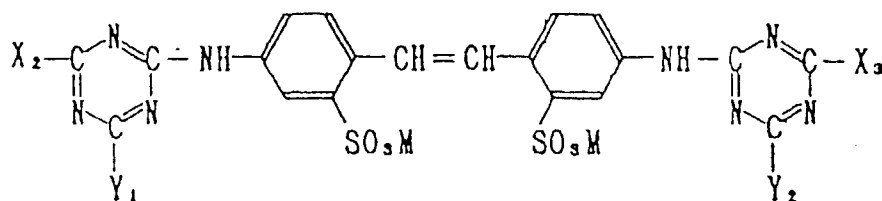


As apparent from Table 6, the object of the invention can be well achieved by the addition of the fluorescent brightener represented by Formula (E).

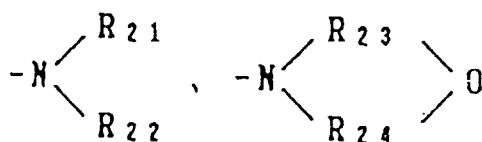
Claims

1. A method of processing a silver halide color photographic light-sensitive material having a silver halide emulsion layer containing silver halide grains having a silver chloride content of not less than 80 mol%, which comprises color-developing the material with a color developer comprising a compound represented by the following Formula E,

Formula (E)



wherein X^2 , X^3 , Y_1 and Y_2 each independently represent a hydroxyl group, halogen atom, alkyl group, aryl group,



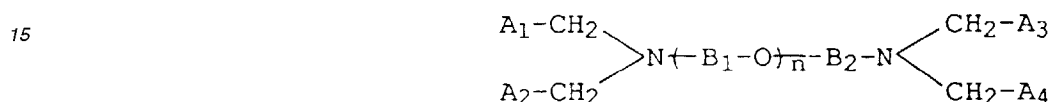
or $-\text{OR}_{25}$, wherein R_{21} and R_{22} each independently represent a hydrogen atom, alkyl group or aryl group; R_{23} and R_{24} each represent an alkylene group; R_{25} represents a hydrogen atom, alkyl group or aryl group; and M represents a cation; processing the color-developed material with a bleaching solution (BL-1) for a processing time of no longer than 40 seconds, the bleaching solution comprising at least one ferric complex salt of a compound of formula [A] or [B]:

Formula [A]



wherein A₁ to A₄, which may be the same or different, each represents -CH₂OH, -COOM or -PO₃M₁M₂ wherein M, M₁ and M₂ each represents a hydrogen atom, an alkali metal atom or an ammonium group, and X represents a substituted or unsubstituted alkylene group having from three to six carbon atoms;

Formula [B]



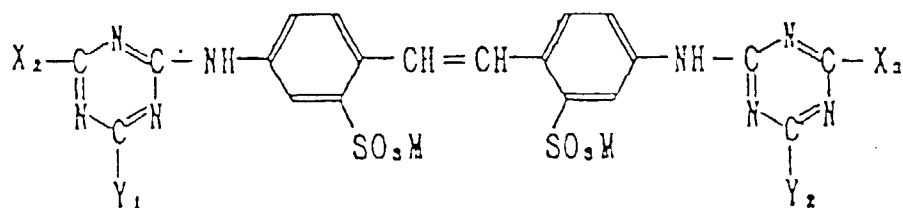
wherein A₁ to A₄ are as defined in Formula [A]; n represents an integer of from 1 to 8; and B₁ and B₂, which may be the same or different, each represents a substituted or unsubstituted alkylene group having from two to five carbon atoms, and wherein the bleaching solution (BL-1) is replenished in an amount of not more than 50 ml/m² of photographic material processed.

2. A method according to claim 1, wherein the bleaching solution (BL-1) contains the ferric complex salt in an amount of from 0.2 to 1.5 mol per liter of solution.
3. A method according to claim 1 or 2, wherein the pH of the bleaching solution (BL-1) is not more than 5.5.
4. A method according to claim 3, wherein the pH of the bleaching solution (BL-1) is from 2.5 to 5.5.
5. A method according to any preceding claim, wherein the bleaching solution (BL-1) is replenished in an amount of not more than 30 ml/m² of photographic material processed.
6. A method according to any preceding claim, wherein a part or the whole of a bleaching solution (BL-2) which has been used independently for processing another kind of silver halide color photographic material is used to replenish the bleaching solution (BL-1).
7. A method according to claim 6, wherein a part or the whole of a bleaching solution used for processing a color photographic negative film is used to replenish the bleaching solution (BL-1), and wherein the photographic material which is processed is a color photographic negative paper.
8. A method according to any one of the preceding claims, wherein the photographic material has a coating weight of silver of not more than 0.75 g/m² of material.

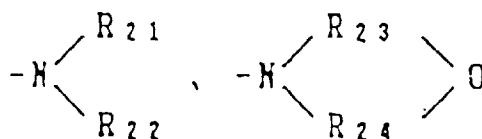
Patentansprüche

1. Verfahren zum Behandeln eines lichtempfindlichen farbphotographischen Silberhalogenidaufzeichnungsmaterials mit einer Silberhalogenidemulsionsschicht, welche Silberhalogenidkörnchen eines Silberchloridgehalts von nicht weniger als 80 Mol-% enthält, umfassend die Farbentwicklung des Aufzeichnungsmaterials mit einem Farbwickler, mit einer Verbindung der folgenden Formel E

Formel (E)

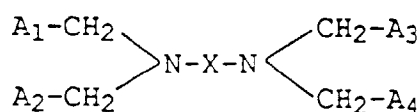


worin X^2 , X^3 , Y_1 und Y_2 jeweils unabhängig voneinander eine Hydroxylgruppe, ein Halogenatom, eine Alkylgruppe, eine Arylgruppe,



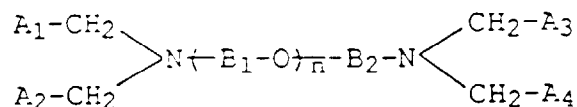
oder -OR₂₅ mit R₂₁ und R₂₂ jeweils unabhängig voneinander gleich einem Wasserstoffatom, einer Alkylgruppe oder einer Arylgruppe, R₂₃ und R₂₄ jeweils gleich einer Alkylengruppe und R₂₅ gleich einem Wasserstoffatom, einer Alkylgruppe oder einer Arylgruppe, bedeuten und M ein Kation darstellt;
und die nicht länger als 40 s dauernde Behandlung des farbentwickelten Aufzeichnungsmaterials mit einem Bleichbad (BL-1), umfassend mindestens ein Eisen(III)komplexsalz einer Verbindung der Formel [A] oder [B]:

Formel [A]



worin A₁ bis A₄, die gleich oder verschieden sein können, jeweils -CH₂OH, -COOM oder -PO₃M₁M₂ mit M, M₁ und M₂ jeweils gleich einem Wasserstoffatom, einem Alkalimetallatom oder einer Ammoniumgruppe bedeuten und X eine gegebenenfalls substituierte Alkylengruppe mit drei bis sechs Kohlenstoffatomen darstellt;

Formel [B]



worin A₁ bis A₄ in gleicher Weise wie bei Formel [A] definiert sind; n eine ganze Zahl von 1 bis 8 bedeutet und B₁ und B₂, die gleich oder verschieden sein können, jeweils für eine gegebenenfalls substituierte Alkylengruppe mit zwei bis fünf Kohlenstoffatomen stehen, wobei das Bleichbad (BL-1) in einer Menge von nicht mehr als 50 ml/m² des behandelten photographischen Aufzeichnungsmaterials ergänzt wird.

2. Verfahren nach Anspruch 1, wobei das Bleichbad (BL-1) das Eisen(III)komplexsalz in einer Menge von 0,2 bis 1,5 mol pro Liter Lösung enthält.
3. Verfahren nach Anspruch 1 oder 2, wobei der pH-Wert des Bleichbades (BL-1) nicht mehr als 5,5 beträgt.
4. Verfahren nach Anspruch 3, wobei der pH-Wert des Bleichbades (BL-1) 2,5 bis 5,5 beträgt.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Bleichbad (BL-1) in einer Menge von nicht mehr

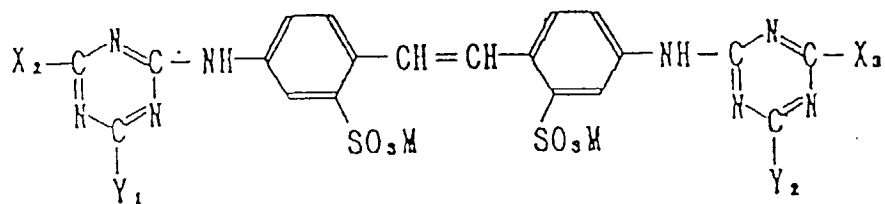
als 30 ml/m² des behandelten photographischen Aufzeichnungsmaterials ergänzt wird.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei ein unabhängig zur Behandlung einer anderen Art eines farbphotographischen Silberhalogenidaufzeichnungsmaterials verwendetes Bleichbad (BL-2) teilweise oder vollständig zur Ergänzung des Bleichbades (BL-1) verwendet wird.
7. Verfahren nach Anspruch 6, wobei ein zur Behandlung eines farbphotographischen Negativfilms verwendetes Bleichbad teilweise oder vollständig zur Ergänzung des Bleichbades (BL-1) verwendet wird und es sich bei dem behandelten photographischen Aufzeichnungsmaterial um ein farbphotographisches Negativpapier handelt.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das photographische Aufzeichnungsmaterial ein Silberauftragsgewicht von nicht mehr als 0,75 g/m² Aufzeichnungsmaterial aufweist.

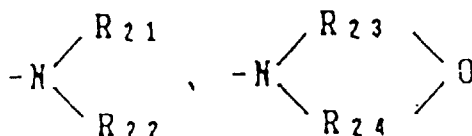
Revendications

1. Procédé de traitement d'un matériau photosensible pour la photographie couleur, à base d'halogénure d'argent, ayant une couche d'émulsion à base d'halogénure d'argent contenant des grains d'halogénure d'argent ayant une teneur en chlorure d'argent qui n'est pas inférieure à 80 % en moles, comprenant le développement couleur du matériau avec un agent de développement couleur comprenant un composé représenté par la formule E suivante

Formule E

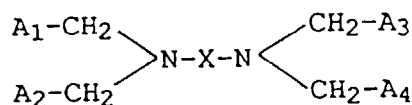


dans laquelle X², X³, Y₁ et Y₂ représentent chacun indépendamment un groupe hydroxyle, un atome d'halogène, un groupe alkyle, un groupe aryle,



ou -OR₂₅, où R₂₁ et R₂₂ représentent chacun indépendamment un atome d'hydrogène, un groupe alkyle ou un groupe aryle; R₂₃ et R₂₄ représentent chacun un groupe alkylène; R₂₅ représente un atome d'hydrogène, un groupe alkyle ou un groupe aryle; et M représente un cation; le traitement du matériau ayant subi un développement couleur avec une solution de décoloration (BL-1) pendant une durée de traitement n'excédant pas 40 secondes, la solution de décoloration comprenant au moins un sel complexe ferrique d'un composé de formule [A] ou [B]:

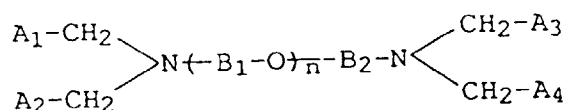
Formule [A]



dans laquelle A₁ à A₄, qui peuvent être identiques ou différents, représentent chacun -CH₂OH, -COOM ou PO₃M₁M₂, où M, M₁ et M₂ représentent chacun un atome d'hydrogène, un atome de métal alcalin ou un groupe

ammonium, et X représente un groupe alkylène substitué ou non substitué, ayant trois à six atomes de carbone ;

Formule [B]



dans laquelle A_1 à A_4 sont tels que définis dans la formule [A] ; n représente un nombre entier de 1 à 8 ; et B_1 et B_2 , qui peuvent être identiques ou différents, représentent chacun un groupe alkylène substitué ou non substitué, ayant deux à cinq atomes de carbone, et où la solution de décoloration est complétée dans une proportion n'excédant pas 50 ml/m² du matériau photographique traité.

2. Procédé selon la revendication 1, dans lequel la solution de décoloration (BL-1) contient le sel complexe ferrique dans une proportion de 0,2 à 1,5 mole par litre de solution.
3. Procédé selon la revendication 1 ou 2, dans lequel le pH de la solution de décoloration (BL-1) n'est pas supérieur à 5,5.
4. Procédé selon la revendication 3, dans lequel le pH de la solution de décoloration (BL-1) est de 2,5 à 5,5.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la solution de décoloration (BL-1) est complétée dans une proportion n'excédant pas 30 ml/m² du matériau photographique traité.
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel une partie ou la totalité de la solution de décoloration (BL-2) qui a été utilisée indépendamment pour traiter un autre type de matériau photosensible pour la photographie couleur, à base d'halogénure d'argent, est utilisée pour compléter la solution de décoloration (BL-1).
7. Procédé selon la revendication 6, dans lequel une partie ou la totalité d'une solution de décoloration utilisée pour le traitement d'une pellicule négative pour la photographie couleur est utilisée pour compléter la solution de décoloration (BL-1) et dans lequel le matériau photographique qui est traité est un papier négatif pour la photographie couleur.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau photographique présente un poids de revêtement d'argent n'excédant pas 0,75 g/m² du matériau.